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## [54] PROCESS AND APPARATUS FOR CONTROLLING TEMPERATURES IN REACTANT CHANNELS

5,193,611 3/1993 Hesselgraves 165/166  
5,316,628 5/1994 Collin et al. 165/166  
5,413,872 5/1995 Faigle 165/166

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## [57] ABSTRACT

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A reactor arrangement and process for indirectly contacting a reactant stream with a heat exchange stream uses an arrangement of corrugated heat exchange plates and a plate containing protrusions between the corrugated plates to control temperature conditions by varying the number and/or the projection of the protrusions between the plates. The reactor arrangement and process of this invention may be used to operate a reactor under isothermal or other controlled temperature conditions. The variation in protrusion arrangements within a single heat exchange section is highly useful in maintaining a desired temperature profile in an arrangement having a cross-flow of heat exchange medium relative to reactants. The protrusion arrangement offers a simplified method to eliminate or minimize the typical step-wise approach to isothermal conditions.

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[52] U.S. Cl. 422/200; 422/198; 165/166; 165/167

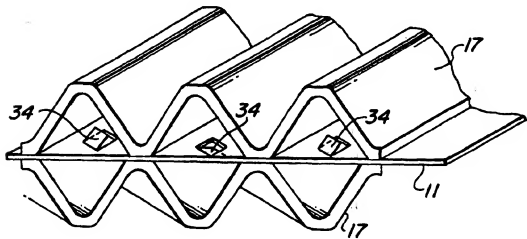
[58] Field of Search 422/198, 200; 165/166, 167

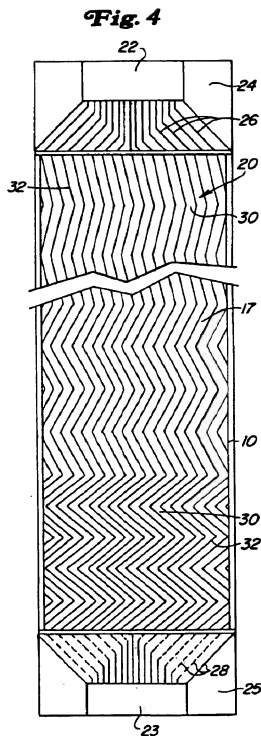
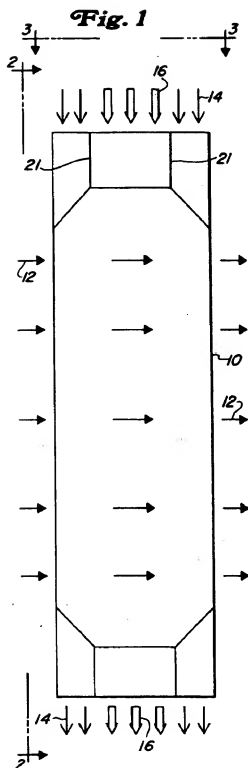
## [56] References Cited

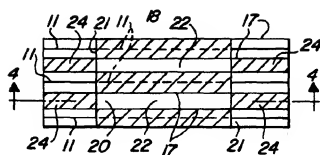
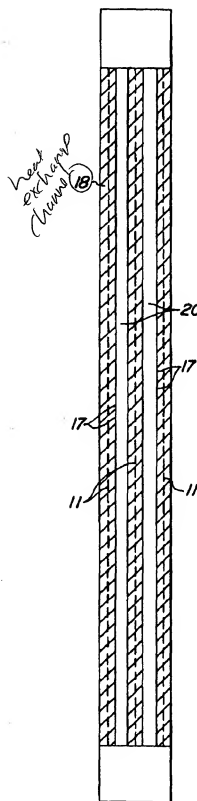
### U.S. PATENT DOCUMENTS

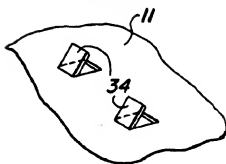
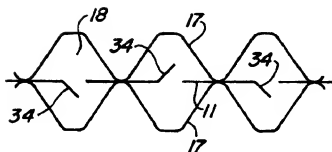
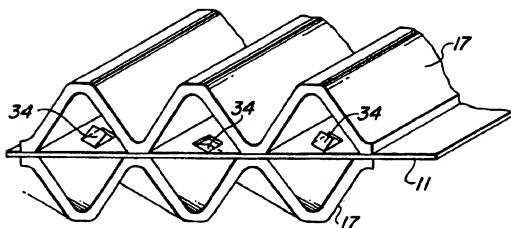
4,693,807 9/1987 Westerman et al. 208/108  
4,973,401 11/1990 Dang Vu et al. 208/134  
5,047,217 9/1991 Dang Vu et al. 422/200  
5,073,352 12/1991 Dang Vu et al. 422/213  
5,114,776 5/1992 Casarotti 165/166  
5,186,909 2/1993 Dang Vu et al. 422/213

17 Claims, 3 Drawing Sheets





**Fig. 3****Fig. 2**

**Fig. 5****Fig. 6****Fig. 7**

# PROCESS AND APPARATUS FOR CONTROLLING TEMPERATURES IN REACTANT CHANNELS

## FIELD OF THE INVENTION

This invention relates to chemical reactors for the conversion of a reaction fluid while indirectly exchanging heat with a heat exchange fluid.

## BACKGROUND OF THE INVENTION

In many industries, like the petrochemical and chemical industries for instance, the processes employ reactors in which chemical reactions are effected in the components of one or more reaction fluids under given temperature and pressure conditions. Many of these reactions generate or absorb heat, to various degrees, and are, therefore, exothermic or endothermic. The heating or chilling effects associated with exothermic or endothermic reactions can positively or negatively affect the operation of the reaction zone. The negative effects can include among other things: poor product production, deactivation of the catalyst, production of unwanted by-products and, in extreme cases, damage to the reaction vessel and associated piping. More typically, the undesired effects associated with temperature changes will reduce the selectivity or yield of products from the reaction zone.

One solution for controlling the changes in temperature associated with the heats of various reactions has been to operate several adiabatic reaction zones with intermediate heating or cooling between the different reaction zones. In each adiabatic reaction stage, all of the heat liberated or absorbed during the reaction is transmitted directly to the reactive fluid and the reactor internals. The degree of heat release and the tolerance for temperature change determines the total number of adiabatic reactor zones required in such arrangements. Each zone or adiabatic stage of reaction adds significantly to the overall cost of such a process due to the equipment expense of adding piping and heaters or coolers for intermediate stages of heat transfer to a reactant that passes through the reaction zones. Therefore the number of adiabatic steps is limited and such systems offer at best a stepwise approach to isothermal or other controlled temperature conditions. Moreover, the breaking up of a reaction zone into a series of reactors with intermediate heating or cooling of reactants, especially interferes with reactor arrangements that have continual addition and withdrawal of catalyst from the reaction zone.

Other solutions to the problem of temperature control under the influence of different heats of reaction have employed direct or indirect heating or cooling within the reaction zone. Direct heating or cooling utilizes a compensating reaction having a directionally different heat requirement that occurs simultaneously with the principal reaction. The counter balancing reaction offsets heat release or heat adsorption from the principal reaction. One of the simplest forms of such an arrangement is an endothermic process that uses oxidation of hydrogen to heat reactants in an endothermic reaction.

Another solution has been the indirect heating of reactants and/or catalysts within a reaction zone with a heating or cooling medium. The most well known catalytic reactors of this type are tubular arrangements that have fixed or moving bed catalysts. The geometry of tubular reactors poses layout constraints that require large reactors or limit throughput.

Indirect heat exchange has also been accomplished using thin plates to define channels that alternately retain catalyst and reactants between a heat transfer fluid for indirectly heating or cooling the reactants and catalysts. Heat exchange plates in these indirect heat exchange reactors can be flat or curved and may have surface variations such as corrugations to increase heat transfer between the heat transfer fluids and the reactants and catalysts. Although the thin heat transfer plates can, to some extent, compensate for the changes in temperature induced by the heat of reaction, the indirect heat transfer arrangements are not able to offer the complete temperature control that would benefit many processes by maintaining a desired temperature profile through a reaction zone.

Many hydrocarbon conversion processes will operate more advantageously by maintaining a temperature profile that differs from that created by the heat of reaction. In many reactions, the most beneficial temperature profile will be obtained by substantially isothermal conditions. In some cases, a temperature profile directionally opposite to the temperature changes associated with the heat of reaction will provide the most beneficial conditions. An example of such a case is in dehydrogenation reactions wherein the selectivity and conversion of the endothermic process is improved by having a rising temperature profile, or reverse temperature gradient through the reaction zone.

A reverse temperature gradient for the purposes of this specification refers to a condition where the change in temperature through a reaction zone is opposite to that driven by the heat input from the reaction. In an endothermic reaction, a reverse temperature gradient would mean that the average temperature of the reactants towards the outlet end of the reaction zone have a higher value than the average temperature of the reactants at the inlet end of the reaction zone. In an opposite manner, a reverse temperature gradient in an exothermic reaction refers to a condition wherein reactants towards the inlet end of the reactor have a higher average temperature than the reactants as they pass toward the outlet end of the reaction section.

It is an object of this invention to provide a reactor that offers greater temperature control of reactants by the indirect heating or cooling of a reaction stream by a heat exchange fluid within a reaction zone.

It is a further object of this invention to provide a process and apparatus used for indirect heat exchange of a reactant stream with a heat exchange stream for controlling the temperature profile through the reaction zone.

Another object of this invention is to provide a process that uses indirect heat exchange with a heat exchange fluid to maintain substantially isothermal conditions or a reverse temperature gradient through a reactor.

## BRIEF SUMMARY OF THE INVENTION

This invention is a chemical reactor and a process for using a chemical reactor that employs an arrangement of heat exchange plates within the reactor that will maintain reactor temperatures within a desired range during the reaction. The heat exchange plates define alternate channels for the heat exchange fluid and the reactants. Heat transfer is controlled in this invention by locating a heat transfer adjustment plate in the center of channels that convey a heat transfer fluid through the reactor. The adjustment plate defines protrusion that extend into the heat transfer channels and reduce or increase turbulence with the channel. Raising or lowering the turbulence in the heat exchange channel

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increases or decreases the heat transfer coefficient across the heat exchange plates that separate the reactant channels from the heat transfer channels. In this manner the degree of indirect heat exchange along the length of the reactor can be adjusted to maintain a desired temperature profile.

The heat adjustment plate is susceptible to a variety of configurations. The only essential requirement is that the plate have a surface that creates a varied amount of turbulence as the heat transfer fluid contacts different portions of the plate. The plate can induce variations in turbulence by changing the surface roughness over different portions of the plate, using a varied number and size of a perforations over the plate. The more effective arrangements of this invention use the adjustment plate to define protrusions that extend from the plate and project into the flow path of the heat exchange fluid.

The number, shape and amount of protrusions can be adjusted over the surface of the plate to provide the desired degree of temperature adjustment within the reactant channels. For example in an endothermic reaction more or larger protrusions are provided in the heat exchange channels that heat the portion of the reactant channels located toward the outlet of the reactor. The increased number of protrusions toward one end of the reactor selectively increases heat exchange at the outlet end of the reactant channels and provides the necessary heat input to maintain a constant temperature throughout the reactant channels. The number of protrusions provided over the plate can be adjusted as needed to suit the endothermicity or exothermicity of the reaction occurring in the reactant channels.

This invention will promote the control of temperatures through a reaction zone. Preferably this invention will maintain the desired inlet and outlet temperatures within 10° F. and more preferably within 5° F. of a desired temperature profile through the reactant channels. Where isothermal conditions are desired the inlet and outlet temperature are equal, such that one requirement of the substantially isothermal conditions described in this invention is that the mean inlet and outlet temperature vary by no more than 10° F. and preferably by no more than 5° F.

A process and catalyst reactor arrangement that uses this invention may employ single or multiple reaction zones within a reactor vessel. The advantage of this invention is that the reactor vessel can provide the desired temperature gradient without intermediate withdrawal and recycling of reactants or heat exchange medium between the inlet and outlet of the reactor. The multiple reaction zones within the reactor vessel can be used to accommodate variations in the heat adjustment plate.

Accordingly, in an apparatus embodiment, this invention is a reactor for controlling temperature profiles in a reaction zone. The reactor includes a plurality of spaced apart heat exchange plates. Each heat exchange plate has an extended length and defines a boundary of a heat exchange flow channel on one side of the plate and a boundary of a reaction flow channel on an opposite side of the plate. Means are provided for passing a reaction fluid along through a plurality of the reaction flow channels defined by the plates along a first flow path and means are provided for passing a heat exchange fluid through a plurality of the heat exchange channels defined by the plates along a second flow path. A heat adjustment plate in each heat exchange channel defines a plurality of protrusions that project into the heat exchange channels. The protrusions have an area of projection into the heat exchange flow channel that varies over the length of the plate to produce varied turbulence across the channels.

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Preferably each heat exchange plate defines corrugations and the heat adjustment plate is sandwiched between the corrugations in the heat exchange channel.

In another embodiment, this invention is a process for controlling the temperature of a reactant stream in a chemical reaction by indirect heat exchange with a heat exchange fluid across a multiplicity of plate elements. The process comprises passing a heat exchange fluid from a heat exchange inlet to a heat exchange outlet through a first set of elongated channels formed by a first side of a plurality of heat exchange plates. A reactant stream passes from a reactant inlet to a reactant outlet through a second set of channels formed by a second side of the heat exchange plates. The process exchanges heat between the heat exchange fluid and the reactant stream by contacting the heat exchange fluid with corrugations formed by the heat exchange plates. In addition to the corrugations the heat exchange fluid in the heat exchange channels contacts a heat adjustment plate that contains a plurality of protrusions to vary the heat transfer coefficient within the heat transfer channels.

The process may be useful in a wide variety of catalytic reactions. This invention is most beneficially applied to catalytic conversion process having high heats of reaction. Typical reactions of this type are hydrocarbon conversion reactions that include: the aromatization of hydrocarbons, the reforming of hydrocarbons, the alkylation of hydrocarbons, the hydrocracking of hydrocarbons, the isomerization of hydrocarbons, the hydrogenation of hydrocarbons, the alkylation of hydrocarbons, the alkylation of aromatic hydrocarbons.

The reaction zones for the process of this invention may indirectly contact the reactants with the heat exchange fluid in any relative direction. Thus, the flow channels and inlet and outlets of the reaction zones may be designed for concurrent, countercurrent, or crossflow of reactant and heat exchange fluid. Preferred process arrangements for practicing this invention will pass reactants in cross-flow to the heat exchange fluid. Cross-flow of reactants is generally preferred to minimize the pressure drop associated with the flow of reactants through the reactor. For this reason, a cross-flow arrangement can be used to provide the reactants with a shorter flow path across the reaction zone.

Effective use of the adjustment plate in a cross-flow arrangement of reactants and heat exchange fluids requires attention to pressure drop considerations. Changing the heat transfer along the path of the reactant stream requires a variation in the protrusions along a path transverse to the flow of the heating medium. Increasing the size or number of protrusions on one side of the heat exchange channels to increase heat transfer can increase the resistance to flow through the same portion of the channel. Increased flow resistance and resulting pressure drop can redistribute fluid flow across the channel and redirect a greater flow of heat exchange fluid back to the portion of the heat exchange channels where less heating is desired. If not considered in the design of the channels or heat adjustment plate this increased flow will increase heat transfer and undo the effect of the increased protrusions. Accordingly in a cross-flow arrangement the protrusions should increase turbulence without adversely redistributing the flow of heat exchange fluid with increased pressure drop. Increasing turbulence independent of pressure drop may be accomplished by adjusting the shape and configuration of the protrusions. Heat transfer is effectively enhanced by using protrusions that direct the heat exchange fluid into impact with surfaces

of the channels and heat transfer plates. Turbulence and pressure drop may be decoupled by using protrusions that maximize the redirection and impact of the heat exchange fluid with plate surfaces at one end of the heat exchange channel and using protrusion that maintain pressure drop without redirection at the other end of the channel. The incorporation of perforations in the protrusions provides another method of increasing turbulence and without raising pressure drop.

The shorter flow path, particularly in the case of the reactant stream contacting heterogeneous catalysts, reduces overall pressure drop of the reactants as they pass through the reactor. Lower pressure drops can have a two-fold advantage in the processing of many reactant streams. Increased flow resistance i.e., pressure drop, can raise the overall operating pressure of a process. In many cases, product yield or selectivity is favored by lower operating pressure so that minimizing pressure drop will also provide a greater yield of desired products. In addition, higher pressure drop raises the overall utility and cost of operating a process.

It is also not necessary to the practice of this invention that each reactant channel contain only one heat adjustment plate. Possible configurations of the reaction section may place two or more heat adjustment plates within each reactant channel to offer greater control to turbulence within a channel.

Additional embodiments, arrangements, and details of the invention are disclosed in the following detailed description of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a catalytic reaction section of this invention showing a preferred direction for the circulation of fluids and catalyst.

FIG. 2 is a side view of the catalytic reaction section taken along lines 2—2 of FIG. 1.

FIG. 3 is a top view of the reactor section of FIG. 1 taken along lines 3—3.

FIG. 4 is a section of the reaction system shown in FIG. 1 taken along line 4—4 of FIG. 3.

FIG. 5 is a section of a heat adjustment plate of this invention.

FIG. 6 is a section of the channels formed by corrugated plates containing the heat adjustment plate of this invention.

FIG. 7 is a perspective view of the channels and heat adjustment plate shown in FIG. 6.

#### DETAILED DESCRIPTION OF THE INVENTION

By its very design, the reactor according to this invention has the advantage of maintaining, with simple means, desired temperature profiles including isothermal or reverse gradient temperature conditions during the flow of the reactive fluid in the reactor, by means of a heat transfer medium. This invention aids in the effective use of catalytic materials by controlling temperatures in a manner that enhances performance of the catalytic reaction.

The process and reactor arrangement may use homogeneous or heterogeneous catalysis. Homogeneous catalyst will typically comprise liquid catalysts that flow through reaction channels along with the reactants and are separated for recovery and recycle outside of the reaction zone. This reactor arrangement provides particular benefits with het-

erogeneous catalysis that are typically retained within the reactant channels by the corrugated plates and permeable members that retain the catalyst but permit the flow of reactants therethrough. In most cases, the heterogeneous catalyst will comprise particulate material retained between the plates and the reactor may be arranged to permit the continuous addition and withdrawal of particulate material while the reactor is on stream.

The type and details of the reactor arrangements contemplated in the practice of this invention is best appreciated by a reference to the drawings. FIG. 1 is a schematic representation of a catalytic reactor section 10 designed to effect a catalytic reaction on a reactant fluid while using indirect heat exchange with a heat transfer fluid to maintain favorable reaction temperatures as the reactant fluid flows through the catalytic reaction section. The catalytic reaction section comprises a stack of heat exchange plates 17 of the type represented in FIGS. 2 and 3. Each plate 17 is stacked in a spaced apart relationship next to adjacent plates 17 to form two circulation systems, the first one for a flow of a reactive fluid 12 and the second one for flow of heat exchange fluid 14. When present a flow of catalyst 16 will also pass through the first circulation system. Together FIGS. 1 through 3 define a specific circulation system, wherein the reactive fluid and the heat exchange fluid respectively, flow in crosswise directions, i.e. perpendicular and through alternate channels formed between adjacent plates 17. In FIG. 1, a reactant fluid passes horizontally in the direction indicated by arrows 12. The heat exchange fluid flows transversely to the reactant fluid in the direction indicated by arrows 14. Catalyst also passes through the reactant channels with the reactants in the direction and at a location indicated by arrows 16. FIG. 2 shows via a side view, the arrangement of alternate heat exchange channels 18 and reactant channels 20 formed by the plurality of heat exchange plates 17. Reactant channels 20 are open at the edge of the reactor to isolate the reactant channels from the heat exchange channels. Where the reactant channels also contain a particulate catalyst material, a suitable screen covers the open sides of reactant channels 20 to retain the catalyst. The sides of heat exchange channels 18 are sealed to confine the heat exchange fluid for vertical flow through the reaction section. FIG. 2 also shows the heat adjustment plate 11 as dashed line centered in the closed off heat exchange channels. The heat exchange plates preferably define continuous channels for both the reactant and the heat exchange fluid over the length and width of the reaction section. The continuous heat exchange channels maintain the heat exchange fluid in contact with the heat adjustment plate over the length of the reaction section.

The same alternate arrangement of heat exchange channels and reactant channels is shown in FIG. 3. As indicated by FIG. 3, the outer ends 19 of the heat exchange channels 18 are open to admit fluid into the heat exchange channels. The outer section 24 of reactant channels 20 are closed off to keep the heat exchange fluid out of the reactant channels. A partition 21 separates the central portion of heat exchange and reactant channels from the outer ends. Inside partition 21 the central portion of heat exchange channels 18 are closed to fluid flow. Closing the center of heat exchange channels 18 permits the center section of the reaction section to receive a particulate catalyst and distribute the catalyst to the open central portion 20 of reactant channels 20. Thus, catalyst passing vertically through the reactant channels enters the reaction section through the central portion 22 of the reactant channels. The vertically flowing reactants and catalyst exit the reaction section through a similar arrange-

ment at the bottom of the reaction section. As shown in FIG. 4, central portion 22 of the reactant channels distributes catalyst to a series of baffles 26 that distribute the catalyst to the reactant channels. A series of baffles 28 at the bottom of reaction section 10 channel catalyst to a central portion 23 of the reactant channels for the withdrawal of catalyst from reaction section 10.

As depicted in FIG. 4, plates 17 preferably have a corrugated surface creating peaks 30 and valleys 32 that separate reactant channels 20 as well as heat exchange channels 18 into subchannels. In a yet further preferred form of this invention, the corrugations of plate 17 may have a varied pitch that further alters heat transfer coefficients down the length of the reactor to provide additional adjustment in the degree of heating or cooling provided by the indirect heat exchange.

Suitable heat exchange plates for this invention will comprise any plates allowing a high heat transfer rate and which are easily secured into a reaction section in a stable configuration that readily retains the heat transfer adjustment plate. The plates may be formed into curves or other configurations, but flat plates are generally preferred for stacking purposes. Thin plates are preferred and typically have a thickness of from 1 to 2 mm. The plates are typically composed ferrous or non-ferrous alloys such as stainless steels.

As depicted in FIG. 4 the preferred form of the invention will a corrugated plate arrangement. The corrugated plates are particularly useful in positioning the heat adjustment plate. Adjacent corrugations are arranged in an alternating pattern so that the peaks of the corrugations contact where the corrugation patterns cross to maintain the spacing between the plates and define an intersecting pattern of diagonal channels. In this manner the general herring bone pattern on the faces of opposing corrugated plates will extend in opposite directions and the opposing plate faces may be placed in contact with each other to form the flow channels and provide structural support to the plate sections.

As shown in FIG. 4 the corrugations may be varied to effect further control of the heat transfer coefficient between the across the heat exchange plates. The variation in the pitch of the corrugations further assists in maintaining a desired temperature profile through the reaction section. The plate arrangement of FIG. 4 represents a typical corrugation pattern for an exothermic or endothermic process. At the upper inlet end the pitch angle of the corrugations is small, i.e. the principle direction of the corrugations approach a parallel alignment with the heat exchange fluid flow. At the lower end of the plate where the heat exchange fluid exits, the pitch angle of the corrugations is wide to increase relative heat transfer, i.e. the principle direction of the corrugations approach a perpendicular or transverse alignment with respect to the heat exchange fluid flow. Corrugation pitch angles can be in a range of from greater than 0° to less than 90° degrees. Typically the corrugation pitch angle from an inlet to an outlet section of a plate will range from about 10° to 80°, and more typically in a range of about 15° to 60°. In a particularly preferred arrangement, the plates will make an angle of less than 30° at the inlet end of the plate and an angle of more than 35° at the outlet end of the plate. The varying corrugations may be formed in a continuous plate section or the plate section of the type shown in FIG. 4 may be made from several plates having corrugations at different pitch angles.

Preferably the reactant channels in which the reactant fluid circulates, includes a heterogeneous catalyst in the form

of particles. The catalyst particles typically comprise grains of a small size. The particles may take on any kind of shape, but usually comprise small spheres or cylinders.

When flowing through reactant channels 20, the reactant fluid undergoes a catalytic reaction accompanied by a liberation or an absorption of heat. The function of the heat exchange fluid circulating in the heat exchange channels is to convey the heat to be added to or removed from the reactant fluid, in order to maintain favorable reaction conditions. Such conditions can again include isothermal conditions during the circulation of the afore-mentioned reactive fluid in the catalytic reactor or a reverse temperature gradient. The heat exchange fluid is either a gas or a liquid, depending on the specific operating conditions of each process.

The specific heat transfer relationship for the plate exchange is established by the fundamental equation expressing heat transfer between two fluids. This relationship is as follows:

$$P=hS\Delta T_{LMTD}$$

where:

P is the amount of heat exchanged, h is the local or overall heat transfer coefficient, S is the heat exchange area between fluids, and LMTD is the logarithmic mean temperature difference.

The logarithmic mean temperature difference is readily determined by the desired temperature difference at any point along the plate.

For a series of corrugated plates defining alternate channels of catalyst particles and heat exchanger fluid, the local or overall heat transfer coefficient can be calculated by using the following equation:

$$h=f(a,e,dp)$$

where a is the pitch angle of the corrugations, e is the distance between two plates 17, and dp is the equivalent diameter of catalyst particles.

Appropriate values of h can be established by modeling or computed using known correlations for establishing heat transfer coefficients over corrugated surfaces and, where present, through particle beds. Correlations for localized heat transfer through particle beds may be found in Leva, Ind. Eng. Chem., 42, 2498 (1950). Correlations for heat transfer along corrugations are presented in AIChE Symposium Series No. 295 Vol. 89 Heat Transfer Atlanta (1993).

The area of exchange between the reactant fluid and the auxiliary fluid can be calculated by using the equation:

$$S=naxL$$

where:  $\epsilon$  is a correction factor for the elongation of the plates resulting from the corrugations, n is the number of plates in contact with both heating and reactant fluids, l is the plate width, and L is the plate length.

By varying the number of plates and the characteristics of the corrugations, especially the pitch angle of the corrugations, the corrugations provide means for maintaining desired temperature conditions in the reactant fluid flow direction.

In addition to control of heat transfer coefficients offered by the heat exchange plates, the primary mechanism taught by this invention for controlling heat transfer between the heat transfer channels and the reactant channels is the heat transfer adjustment plate 11. The function of the heat transfer adjustment plate is to vary the turbulence of the heat



exchange fluid passing through the heat transfer channels. The plate is formed or retains elements on its surface that are irregular in shape and induce the desired degree of turbulence at specific locations in the heat transfer channels. The configuration of the irregularities for inducing turbulence can take on a variety of different shapes. Typically, the irregularities will be in the form of protrusions that will project outwardly from the plate into the flow path of the heat exchange fluid. As the heat exchange fluid contacts the projecting protrusions, turbulence is raised and heat transfer between the fluid and the surface of the heat transfer plate is increased. The change in the heat transfer coefficient at a given location of the channels by the increased degree of turbulence is readily calculated by methods well known to those skilled in the art. Accordingly, the variation in the heat transfer coefficient achieved by the pattern of surface irregularities on the heat transfer adjustment plate can be readily calculated or determined experimentally.

In a preferred form of the invention, the surface irregularities are formed by punching laterally extending tabs from the heat adjustment plate, material and bending the tabs into the flow path of the heat exchange fluid. FIG. 5 shows a heat adjustment plate 11 from which tabs 34 have been bent outwardly. Adjustment of the turbulence induced by the tabs can be varied by changing the projection of the tabs into the flow path of the heat exchange fluid or increasing the number of tabs in portions of the heat exchange channels where additional heat transfer is desired.

FIG. 6 depicts a typical cross-section of a corrugated heat exchange channel containing a heat adjustment plate of the type depicted in FIG. 5. The corrugation peaks of heat exchange plate 17 retain heat adjustment plate 11 in a sandwich configuration. Heat adjustment plate 11 generally crosses through the center of heat adjustment channels 18. Heat adjustment tabs 34 occupy a central portion of the heat adjustment channel 18. Preferably heat adjustment tabs 34 will not contact the heat adjustment plate 17. Suitable heat adjustment plates can have an impermeable surface to prevent exchange of heat transfer fluid across the heat adjustment plate. Preferably, the heat adjustment plate will have perforations associated with the protrusions to permit passage of the heat exchange fluid across the heat adjustment plate. FIG. 6 also shows a preferred form for the tabs where alternate tabs project away from opposite sides of heat adjustment plate 11. FIG. 7 depicts a three dimensional arrangement of the channels and heat adjustment plate shown in FIG. 6.

Heat adjustment plate 11 will preferably comprise a thin plate having a thickness similar to that of the heat transfer plates. The heat adjustment plate operates in two ways to provide additional heat transfer across the heat exchange plates. Increased turbulence from the protrusions on the heat adjustment plate will indirectly increase heat transfer between the heat transfer fluid and the heat transfer plate. In addition, heat and adjustment plate 11 provides an additional surface for direct conduction of heat from the heat transfer fluid to the adjustment plate and from the adjustment plate to the points of contact with the heat transfer plates.

This invention may be particularly useful in many hydrocarbon conversion processes. Catalytic reforming is one such well established hydrocarbon conversion process employed in the petroleum refining industry for improving the octane quality of hydrocarbon feedstocks, the primary product of reforming being motor gasoline. The art of catalytic reforming is well known and does not require extensive description herein. Briefly, in catalytic reforming, a feedstock is admixed with a recycle stream comprising

hydrogen and contacted with catalyst in a reaction zone. The usual feedstock for catalytic reforming is a petroleum fraction known as naphtha and having an initial boiling point of about 180° F. (80° C.) and an end boiling point of about 400° F. (205° C.). The catalytic reforming process is particularly applicable to the treatment of straight run gasoline comprised of relatively large concentrations of naphthenic and substantially straight chain paraffinic hydrocarbons, which are subject to aromatization through dehydrogenation and/or cyclization reactions. Reforming may be defined as the total effect produced by aldehydogenation of cyclohexanes and dehydroisomerization of alkylcyclopentanes to yield aromatics, aldehydogenation of paraffins to yield olefins, dehydrocyclization of paraffins and olefins to yield aromatics, isomerization of n-paraffins, isomerization of alkylcycloparaffins to yield cyclohexanes, isomerization of substituted aromatics, and hydrocracking of paraffins. Further information on reforming processes may be found in, for example, U.S. Pat. No. 4,119,526 (Peters et al.); 4,409,095 (Peters); and 4,440,626 (Winter et al.), the contents of which are herein incorporated by reference.

A catalytic reforming reaction is normally effected in the presence of catalyst particles comprised of one or more Group VIII noble metals (e.g., platinum, iridium, rhodium, palladium) and a halogen combined with a porous carrier, such as a refractory inorganic oxide. The halogen is normally chlorine. Alumina is a commonly used carrier. The preferred alumina materials are known as the gamma, eta and theta alumina with gamma and eta alumina giving the best results. An important property related to the performance of the catalyst is the surface area of from 100 to about 500 m<sup>2</sup>/g. The particles are usually spheroidal and have a diameter of from about 1/4 inch to about 1/2 inch (1.5-3.1 mm), though they may be as large as 1/4 inch (6.35 mm). A preferred catalyst particle diameter is 1/4 inch (3.1 mm). During the course of a reforming reaction, catalyst particles become deactivated as a result of mechanisms such as the deposition of coke on the particles; that is, after a period of time in use, the ability of catalyst particles to promote reforming reactions decreases to the point that the catalyst is no longer useful. The catalyst must be reconditioned, or regenerated, before it can be reused in a reforming process.

In preferred form, the reforming operation will employ a moving bed reaction zone and regeneration zone. The present invention is applicable to moving bed and fixed bed zones. In a moving bed operation, fresh catalyst particles are fed to a reaction zone by gravity. Catalyst is withdrawn from the bottom of the reaction zone and transported to a regeneration zone where a multi-step regeneration process is used to recondition the catalyst to restore its full reaction promoting ability. Catalyst flows by gravity through the various regeneration steps and then is withdrawn from the regeneration zone and furnished to the reaction zone. Movement of catalyst through the zones is often referred to as continuous though, in practice, it is semicontinuous. By semicontinuous movement is meant the repeated transfer of relatively small amounts of catalyst at closely spaced points in time. A moving bed system has the advantage of maintaining production while the catalyst is removed or replaced.

Another preferred hydrocarbon conversion process is the alkylation of aromatic hydrocarbons. In aromatic alkylation suitable aromatic feed hydrocarbons for this invention include various aromatic substrates. Such substrates can be benzene or alkylated aromatic hydrocarbons such as toluene. The acyclic feed hydrocarbon or alkylating agent that may

be used in the alkylation reaction zone also encompasses a broad range of hydrocarbons. Suitable alkylating agents include monoolefins, diolefins, polyolefins, acetylenic hydrocarbons and other substituted hydrocarbons but are preferably  $C_2-C_4$  hydrocarbons. In the most preferred form of this invention, the alkylation agent will comprise  $C_2-C_4$  monoolefins.

A wide variety of catalysts can be used in the alkylation reaction zone. The preferred catalyst for use in this invention is a zeolite catalyst. The catalyst of this invention will usually be used in combination with a refractory inorganic oxide binder. Preferred binders are alumina or silica. Preferred alkylation catalysts are a type Y zeolite having an alumina or silica binder or a beta zeolite having an alumina or silica binder. The zeolite will be present in an amount of at least 50 wt. % of the catalyst and more preferably in an amount of at least 70 wt. % of the catalyst.

The alkylation reaction zone can operate under a broad range of operating conditions. Temperatures usually range from 100° C. to 325° C. with the range of about 150°-275° C. being preferred. Pressures can also vary within a wide range of about 1 atmosphere to 130 atmospheres. Since liquid phase conditions are generally preferred within the reaction zone, the pressure should be sufficient to maintain the reactants in such phase and will typically fall in a range of from 10 to 50 atmospheres. Reactants generally pass through the alkylation zone at a mass flow rate sufficient to yield a liquid hourly space velocity from 0.5 to 50  $hr^{-1}$  and especially from about 1 to 10  $hr^{-1}$ .

The alkylation zone is ordinarily operated to obtain an essentially complete conversion of the alkylating agent to monoalkylate and polyalkylate. To achieve this effect, additional aromatic substrate will usually be charged to the reaction zone. Thus, the feed mixtures are introduced into the reaction zone at a constant rate and a molecular ratio of about 1:1 to 20:1 aromatic substrate to alkylating agent with a ration of about 2:1 to 10:1 being preferred. As a result, in addition to product there will usually be a substantial amount of unreacted aromatic substrate that is removed with the product stream from the alkylation reaction zone. Additional details of aromatic alkylation processes can be found in U.S. Pat. No. 5,177,285, the contents of which are hereby incorporated by reference.

Catalytic dehydrogenation is another example of an endothermic process that advantageously uses the process and apparatus of this invention. Briefly, in catalytic dehydrogenation, a feedstock is admixed with a recycle stream comprising hydrogen and contacted with catalyst in a reaction zone. Feedstocks for catalytic dehydrogenation are typically petroleum fractions comprising paraffins having from about 3 to about 19 carbon atoms. Particular feedstocks will usually contain light or heavy paraffins. For example a usual feedstock for producing a heavy dehydrogenation products will comprise paraffins having 10 or more carbon atoms. The catalytic dehydrogenation process is particularly applicable to the treatment of hydrocarbon feedstocks containing substantially paraffinic hydrocarbons which are subject to dehydrogenation reactions to thereby form olefinic hydrocarbon compounds.

A catalytic dehydrogenation reaction is normally effected in the presence of catalyst particles comprised of one or more Group VIII noble metals (e.g., platinum, iridium, rhodium, palladium) combined with a porous carrier, such as a refractory inorganic oxide. Alumina is a commonly used carrier. The preferred alumina materials are known as the gamma, eta and theta alumina with gamma and eta alumina giving the best results. Preferably, the carrier will have a

surface area of from 100 to about 500  $m^2/g$ . The particles are usually spheroidal and have a diameter of from about  $1/16$ th inch (1.5-3.1 mm), though they may be as large as  $1/4$ th inch (6.35 mm). Generally, the catalyst particles have a chloride concentration of between 0.5 and 1 weight percent. During the course of a dehydrogenation reaction, catalyst particles also become deactivated as a result of coke deposition and require regeneration, similar to that described in conjunction with the reforming process; therefore, in preferred form, the dehydrogenation process will again employ a moving bed reaction zone and regeneration zone.

Dehydrogenation conditions include a temperature of from about 400° to about 900° C., a pressure of from about 0.01 to 10 atmospheres and a liquid hourly space velocity (LHSV) of from about 0.1 to 100  $hr^{-1}$ . Generally, for normal paraffins, the lower the molecular weight the higher the temperature required for comparable conversions. The pressure in the dehydrogenation zone is maintained as low as practicable, consistent with equipment limitations, to maximize the chemical equilibrium advantages. The preferred dehydrogenation conditions of the process of this invention include a temperature of from about 400°-700° C., a pressure from about 0.1 to 5 atmospheres, and a liquid hourly space velocity of from about 0.1 to 100  $hr^{-1}$ .

The effluent stream from the dehydrogenation zone generally will contain unconverted dehydrogenatable hydrocarbons, hydrogen and the products of dehydrogenation reactions. This effluent stream is typically cooled and passed to a hydrogen separation zone to separate a hydrogen-rich vapor phase from a hydrocarbon-rich liquid phase. Generally, the hydrocarbon-rich liquid phase is further separated by means of either a suitable selective adsorbent, a selective solvent, a selective reaction or reactions or by means of a suitable fractionation scheme. Unconverted dehydrogenatable hydrocarbons are recovered and may be recycled to the dehydrogenation zone. Products of the dehydrogenation reactions are recovered as final products or as intermediate products in the preparation of other compounds.

The dehydrogenatable hydrocarbons may be admixed with a diluent gas before, while, or after being passed to the dehydrogenation zone. The diluent material may be hydrogen, steam, methane, carbon dioxide, nitrogen, argon and the like or a mixture thereof. Hydrogen is the preferred diluent. Ordinarily, when a diluent gas is utilized as the diluent, it is utilized in amounts sufficient to ensure a diluent gas to hydrocarbon mole ratio of about 0.1 to about 20, with best results being obtained when the mole ratio range is about 0.5 to 10. The diluent hydrogen stream passed to the dehydrogenation zone will typically be recycled hydrogen separated from the effluent from the dehydrogenation zone in the hydrogen separation zone.

Water or a material which decomposes at dehydrogenation conditions to form water such as an alcohol, aldehyde, ether or ketone, for example, may be added to the dehydrogenation zone, either continuously or intermittently, in an amount to provide, calculated on the basis of equivalent water, about 1 to about 20,000 weight ppm of the hydrocarbon feed stream. About 1 to about 10,000 weight ppm of water addition gives best results when dehydrogenating paraffins having from 6 to 30 more carbon atoms. Additional information related to the operation of dehydrogenation catalysts, operating conditions, and process arrangements can be found in U.S. Pat. Nos. 4,677,237; 4,880,764 and 5,087,792, the contents of which are hereby incorporated by reference.

What is claimed is:

1. A reactor for controlling temperature profiles in a reaction zone, said reactor comprising:

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a plurality of spaced apart heat exchange plates with each plate having an extended length and defining a boundary of a heat exchange flow channel on one side of said plate and a boundary of a reaction flow channel on an opposite side of said plate and each plate defining corrugations;

means for passing a reaction fluid through a plurality of said reaction flow channels defined by said plates along a first flow path;

means for passing a heat exchange fluid through a plurality of said heat exchange channels defined by said plates along a second flow path; and,

a heat adjustment plate sandwiched between said corrugations in said heat exchange channels said heat adjustment plate defining a plurality of protrusions that project into said heat exchange channels, said protrusions having an area of projection into said heat exchange flow channels that varies over the length of said heat adjustment plate to produce varied turbulence across said channels.

2. The reactor of claim 1 wherein said first flow path is perpendicular to said second flow path.

3. The reactor of claim 1 wherein said heat adjustment plate is discontinuous and comprises a first plate section having a greater area of protrusion projection than a second plate section.

4. The reactor of claim 1 wherein said heat adjustment plate is continuous and the area said protrusions increases along one direction of said plate.

5. The reactor of claim 1 wherein the projection area of said protrusions varies by varying the number of protrusions.

6. The reactor of claim 1 wherein the projection area of said protrusions varies by varying size of said protrusions.

7. The reactor of claim 1 wherein said heat adjustment plate is perforated.

8. The reactor of claim 7 wherein said protrusions comprise bent tabs punched from said heat adjustment plate.

9. The reactor of claim 1 wherein said protrusion are on both sides of said plate.

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10. The reactor of claim 1 wherein said reactor includes means for retaining catalyst in said reaction flow channels.

11. A process for controlling the temperature of a reactant stream in a chemical reaction by indirect heat exchange with a heat exchange fluid across a multiplicity of plate elements, said process comprising:

a) passing a heat exchange fluid from a heat exchange inlet to a heat exchange outlet through a first set of elongated channels formed by a first side of a plurality of heat exchange plates;

b) passing a reactant stream from a reactant inlet to a reactant outlet through a second set of channels formed by a second side of said heat exchange plates;

c) exchanging heat between said heat exchange fluid and said reactant stream by contacting said heat exchange fluid with corrugations formed by said heat exchange plates; and,

d) contacting said heat exchange fluid in said heat exchange channels with a heat adjustment plate containing a plurality of protrusions to vary the heat transfer coefficient within said heat transfer channels.

12. The process of claim 11 wherein said reactor retains a heterogeneous catalyst between said heat transfer plates.

13. The process of claim 11 wherein said heat exchange fluid is passed through said heat transfer plates in a transverse flow path relative to said reactant stream.

14. The process of claim 11 wherein said protrusions increase in number through said heat exchange channel.

15. The process of claim 11 wherein said reactant stream comprises hydrocarbons.

16. The process of claim 11 wherein the average temperature of the reactant stream at the reactant inlet is within 10° F. of the average temperature of the reactant stream at the reactant outlet.

17. The process of claim 15 wherein said catalytic reaction is a reforming reaction, aromatization reaction or an aromatic alkylation reaction.

\* \* \* \* \*

# United States Patent [19]

Toy da et al.

[11] 3,925,441

[45] Dec. 9, 1975

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[54] ISOTHERMAL SULFONATION PROCESS

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[58] Field of Search ..... 260/513 T, 505 S, 458,  
260/457, 460, 459, 456 R, 456 P

[56] References Cited

## UNITED STATES PATENTS

2,923,728 2/1960 Falk et al. .... 260/513 R

## FOREIGN PATENTS OR APPLICATIONS

2,138,038 3/1972 Germany ..... 260/513 R

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[57]

## ABSTRACT

In the process for sulfonation by contacting a falling thin film stream of organic compound with a stream of SO<sub>2</sub>-inert gas in parallel, an improved process for isothermal sulfonation producing sulfonates of high quality, which comprises making a SO<sub>2</sub>-containing cooling gas (wherein the SO<sub>2</sub> content is 1 to 20 wt.% relative to the whole amount of SO<sub>2</sub> to be employed) in the amount of about 2 to 12 times (by volume) as much as the total amount of said stream of SO<sub>2</sub>-inert gas flow in parallel between said falling thin film stream of organic compound and said stream of SO<sub>2</sub>-inert gas.

2 Claims, No Drawings

## ISOTHERMAL SULFONATION PROCESS

## BACKGROUND OF THE INVENTION

## a. Field of the Invention

The present invention relates to an improvement of the process for sulfonation by contacting a falling thin film stream of organic compound with a stream of SO<sub>2</sub>-inert gas in parallel. The term "sulfonation" herein means the so-called sulfonation and sulfation.

## b. Description of the Prior Art

The known processes of sulfonation vary depending on the properties and structures of hydrocarbon, etc., to be subjected to sulfonation as well as the kinds of articles to be manufactured therefrom, and sulfonation by the use of sulfur trioxide is one of the typical means. This sulfur trioxide can theoretically complete the addition reaction rapidly and quantitatively, so that it is a very effective sulfonating agent and has been generally utilized for this purpose. But, sulfur trioxide, when employed as it is, will generate extreme heat resulting in various side reactions, and, therefore, diluting it with air or an inert gas prior to application thereof has been widely practiced.

Even in the case of application of SO<sub>2</sub> gas diluted with an inert gas, however, the velocity of sulfonation is so high that the greater part of sulfonation is accomplished at the early stage of reaction, and as this reaction is a strong exothermic reaction, there occurs a peak of temperature at the early stage of reaction, causing side reactions, discoloring of the product, lowering of the conversion rate and generation of the mist within the waste gas.

To cope with the foregoing disadvantages and particularly to prevent the occurrence of the peak of temperature as described above, the inventors have previously proposed in German patent publication OLS-2,138,038 a process comprising introducing an inert cooling gas such as air in the amount of 2 to 12 times by volume as much as the total amount of SO<sub>2</sub>-inert gas between a thin film stream of the organic material and a stream of SO<sub>2</sub>-inert gas in parallel therewith. According to this prior process, though progress of the sulfonation reaction can be controlled to a considerable extent by virtue of the diffusion and permeation or diffusion development of SO<sub>2</sub> gas into the reaction mixture entering the velocity controlling step, the reaction at the early stage is so slow that it takes time, even though a relatively small amount, for the material introduced into the reaction zone to attain the desired temperature, and it has been impossible to obtain satisfactory effects also in respect of the color of the product, the conversion rate and the generation of by-products. Especially in the case of employing an  $\alpha$ -olefin as the organic starting material, there has been observed a tendency for 2-hydroxy alkane sulfonate to occur, which is an undesirable by-product in respect to detergents. Further, in the case of a organic material having a relatively high melting point, it has been accompanied by such difficulty that a portion of the organic material would become solidified and adhere to the inside wall surface of the sulfonator.

## SUMMARY OF THE INVENTION

One object of the present invention is to eliminate the foregoing defects in the prior art and to provide a process which provides a sulfonated product free from discoloring and from by-products, at a high conversion

rate, by making it possible to raise the reaction temperature to a desired temperature immediately after the start of the reaction without said peak of temperature.

Another object of the present invention is to provide an isothermal sulfonation process capable of reducing the generation of mist within the waste gas.

A further object of the present invention is to provide an isothermal sulfonation process capable of preventing adhesion of the product to the inside of the sulfonator even in the case of employing a organic material having a relatively high melting point.

The word "immediately" herein signifies the time necessary for the reactant flowing to the extent of less than about 7% of the full length of the reaction zone from the point of contact (the period of this time is practically immeasurable, but is presumed to be 5% or thereabouts relative to the total reaction time).

The present invention relates to an isothermal sulfonation process as an improvement in the process for sulfonation by flowing downwardly a thin film stream of organic compound together with a stream of SO<sub>2</sub>-inert gas, causing said streams to run in parallel, characterized in that a SO<sub>2</sub>-containing cooling gas (wherein the SO<sub>2</sub> content is 1 to 20 wt.% relative to the whole amount of SO<sub>2</sub> used) in the amount of about 2 to 12 times (by volume) as much as the total volume of said stream of SO<sub>2</sub>-inert gas, is introduced in parallel between said thin film stream of organic compound and said stream of SO<sub>2</sub>-inert gas.

The present method is applicable to any type of film sulfonation apparatus such as double-cylinder type, flat plate type, etc., as well as one combining a plurality thereof.

As the starting organic compound to be sulfonated, various olefins (namely,  $\alpha$ -olefin, inner olefin and vinylidene-type olefin) having 8 to 30 carbon atoms, alkyl benzene having 8 to 15 carbon atoms, aliphatic alcohol having 8 to 24 carbon atoms, alkylene oxide derivatives of aliphatic alcohol having 8 to 22 carbon atoms, alkylene oxide derivatives of alkyl phenol having 8 to 15 carbon atoms, etc. are applicable. These organic compounds are employed in the form of a falling thin film stream, and the temperature thereof at the time of being introduced into the reaction zone is usually in the range of 10° to 45°C, though it varies with the kind of organic material.

As for the cooling gas employed for the SO<sub>2</sub>-containing cooling gas, it can be either identical with or different from the gas used in said SO<sub>2</sub>-inert gas stream as long as it is an inert gas, and the applicable gases include, for instance, air, nitrogen and carbon dioxide gas. The content of SO<sub>2</sub> in this SO<sub>2</sub>-containing cooling gas is in the range of 1 to 20 wt.%-preferably 3 to 15 wt.%-relative to the whole amount of SO<sub>2</sub> employed. However, when said SO<sub>2</sub> content is less than 1 wt.%, the thin film stream of the reacting material immediately after the start of reaction fails to attain the desired temperature while when said SO<sub>2</sub> content is more than 20 wt.%, occurrence of the peak of the rise in temperature as mentioned above is unavoidable, caused by over sulfonation; so that both cases are undesirable.

On the other hand, the concentration of SO<sub>2</sub> gas per se in the SO<sub>2</sub>-containing cooling gas is in the range of about 0.01 to 2% by volume-preferably in the range of about 0.02 to 1% by volume, but is not particularly limited. This SO<sub>2</sub>-containing cooling gas is introduced into the reaction zone to the extent of about 2 to 12 times by volume-preferably about 2 to 7 times by volume-as

much as the total amount of the SO<sub>2</sub>-inert gas employed, at a temperature of about 10° to 40°C and at a velocity substantially the same to about 1/1.4 times as much as that of the stream of SO<sub>2</sub>-inert gas. In the case of the amount of SO<sub>2</sub>-containing cooling gas is less than about 2 times as much as the total amount of said SO<sub>2</sub>-inert gas, occurrence of the peak of rise in temperatures as mentioned above is un-avoidable, so that the initially intended isothermal sulfonation reaction fails to occur, while if the amount of said cooling gas is more than about 12 times as much as the total amount of said SO<sub>2</sub>-inert gas, the contact of the organic material and SO<sub>2</sub> at a desired position is insufficient, so that such disadvantages as retardation of reaction, etc. are caused.

As for the SO<sub>2</sub>-containing inert gas for use in the present invention, any of the conventional ones is applicable. To be precise, the concentration of SO<sub>2</sub> therein is in the range of about 3 to 15% by volume, the velocity for introducing it into the reaction zone is in the range of about 20 to 100 m/sec — preferably about 30 to 80 m/sec, and the temperature thereof at the time of being introduced into the reaction zone is in the range of 20° to 50°C.

According to the process of the present invention, the sulfonation reaction is so advantageously effected that occurrence of undesirable side reactions, generation of coloring matters therein can be controlled, resulting in a product of high quality. Besides, as the chance of the product getting colored is minimized, the bleaching process in the after-treatment can be dispensed with. Further, as the present invention renders the reaction surface of the film of the reactant regulable, generation of mist is markedly decreased, and the reaction can be efficiently effected, thereby achieving not only an increase in yield but also economy of the sulfonating agent. Moreover, the effect of reducing the mist within the waste gas is highly contributive to the prevention of air pollution. Therefore, the industrial merits of the present invention are tremendous.

Hereunder are given some examples embodying the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### EXAMPLE 1.

$\alpha$ -olefin (C<sub>13-15</sub>) obtained through wax cracking was employed as the organic material and it was made into a film stream by use of a falling thin film type sulfonator (length of reaction zone: 2 m) cooled with a cooling water at 20°C and contacted with a stream of SO<sub>2</sub>-air and a stream of SO<sub>2</sub>-containing cooling air flowing parallel thereto under the following conditions, to effect the reaction.

In this case, the velocity of the stream of SO<sub>2</sub>-containing cooling air was set to be about the same as that of the stream of SO<sub>2</sub>-air, and the desired reaction temperature (namely, the temperature of thin film at various places inside the apparatus as measured with a thermocouple having the outside diameter of 0.2 mm) was set at 50°C when the feed rate of organic material was 140 Kg/m.hr and at 60°C when said feed was 250 Kg/m.hr. The molar ratio of SO<sub>2</sub> (relative to the starting material) was set at 1.14.

temperature of air employed:  
cooling air and SO<sub>2</sub>-containing cooling air : 25°C

-continued

SO <sub>2</sub> -containing air	: 40°C
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The amount of SO<sub>2</sub> for use in SO<sub>2</sub>-containing cooling air was set to be 5 wt.% relative to the whole amount of SO<sub>2</sub> employed.

	Concentration of SO <sub>2</sub> gas	Conditions for present example (feed rate of organic material)	Feed rate of gas	Velocity of gas stream
SO <sub>2</sub> -air stream	7.3 vol. %	(140 Kg/m.hr)	0.85 Nm <sup>3</sup> /min	65 m/sec
	12.8 vol. %	(250 Kg/m.hr)		
SO <sub>2</sub> -containing cooling gas stream	0.17 vol. %	(140 Kg/m.hr)	2.15 Nm <sup>3</sup> /min	65 m/sec
	0.30 vol. %	(250 Kg/m.hr)		

Further, for the purpose of comparison, a similar reaction was effected by a stream of cooling air not containing SO<sub>2</sub> (hereinafter called 'cooling air stream' for short) instead of said stream of SO<sub>2</sub>-containing cooling air.

	Concentration of SO <sub>2</sub> gas	Conditions for comparative example (feed rate of organic material)	Feed rate of gas	Velocity of gas stream
SO <sub>2</sub> -air stream	8.1 vol. %	(140 Kg/m.hr)	0.85 Nm <sup>3</sup> /min	65 m/sec
	13.4 vol. %	(250 Kg/m.hr)		
cooling air stream	—	—	2.15 Nm <sup>3</sup> /min	65 m/sec

The measured temperature of the thin film stream of the reactant was as shown in Table 1.

Table 1

	Distances between measurement spot and SO <sub>2</sub> -feeding nozzle	Temperature of thin film stream (°C)	Temperature of thin film stream (°C)
		feed rate of organic material being 140Kg/m.hr	feed rate of organic material being 250Kg/m.hr
	(cm)	(°C)	(°C)
comparative example	7	27	28
	13	35	41
	20	45	58
	35	53	64
	200	45	50
	(cm)	(°C)	(°C)
present example	7	39	30
	13	46	60
	20	50	63
	35	52	66
	200	45	50

The properties (after neutralization and hydrolysis) of the olefin sulfonate obtained in the sulfonation test in the case of feeding the material at the rate of 140 Kg/m.hr\* were as shown in Table 2.

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Table 2

	Comparative example	Present example
unreacted oil content (petroleum ether extract) (active basis) (wt.%)	3.50	3.48
Coloring (5% concentration) (Absorbance (or light of absorption): 10 mm cell, 420 mμ)	0.530**	0.48
Content of disulfonate (active basis) (wt.%)	8.2	8.2
Condition when dissolved in water (25°C)	somewhat turbid with whiteness	clear

\*In the following Examples 2-6, the feed of organic material was also set at 140 Kg/hr.

\*\*Measurement was conducted after filtering with a 0.45μ-milliporefilter.

## EXAMPLE 2.

Sulfonation was effected by applying the same procedures as in Example 1 (including the comparative example; the same applies hereinafter down to Example 6) except for the following modification of the conditions. The result was shown in Table 3.

material: α-olefin having 16 carbon atoms as obtained through Ziegler's method (or process)  
stream of SO<sub>2</sub>-air: concentration SO<sub>2</sub> gas = 7.6 vol.%  
stream of SO<sub>2</sub>-containing cooling air:  
amount of SO<sub>2</sub> employed (relative to the whole amount employed): 7 wt.%  
concentration of SO<sub>2</sub> gas: 0.25 vol.%

Table 3

	Com- parative example	Present example
temperature of film stream at a point 13 cm away from SO <sub>2</sub> -feeding nozzle (°C)	36	50
unreacted oil content (petroleum ether extract) (active basis) (wt.%)	2.60	2.52
coloring (5% concentration) (Absorbance: 10 mm cell, 420 mμ)	0.075	0.070
content of disulfonate (active basis) (wt.%)	7.1	6.8
condition when dissolved in water (°C)	somewhat turbid with whiteness	clear

## EXAMPLE 3

Sulfonation was effected by applying the same procedures as in Example 1 except for the following modification of the conditions. The result was as shown in Table 4.

organic material: α-olefin having 14 carbon atoms, obtained through Ziegler's method  
molar ratio of SO<sub>2</sub> (relative to material): 1.00  
stream of SO<sub>2</sub>-air: concentration of SO<sub>2</sub> gas = 7.4 vol.%  
stream of SO<sub>2</sub>-containing cooling air:  
amount of SO<sub>2</sub> employed (relative to the whole amount employed): 5 wt.%  
concentration of SO<sub>2</sub> gas: 0.18 vol.%

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Table 4

	Com- parative example	Present example
temperature of film stream at a point 13 cm away from SO <sub>2</sub> -feeding nozzle (°C)	38	50
unreacted oil content (petroleum ether extract) (active basis) (wt.%)	6.20	5.75
coloring (5% concentration) (absorbance: 10 mm cell, 420 mμ)	0.030	0.020
content of disulfonate (active basis) (wt.%)	2.0	2.0
condition when dissolved in water (25°C)	turbid with whiteness	clear

## EXAMPLE 4

Sulfation was effected by applying the same procedures as in Example 1 except for the following modification of the conditions. The result was as shown in Table 5.

organic material: condensation product of C<sub>10</sub> alcohol with 3 mol of ethylene oxide (mean molecular weight: 330)  
molar ratio of SO<sub>2</sub> (relative to organic material): 1.03  
stream of SO<sub>2</sub>-air: concentration of SO<sub>2</sub> gas = 4.5 vol.%  
stream of SO<sub>2</sub>-containing cooling air:  
amount of SO<sub>2</sub> employed (relative to the whole amount employed): 14 wt.%  
concentration of SO<sub>2</sub> gas: 0.30 vol.%  
temperature of cooling water: 25°C  
velocity of stream of SO<sub>2</sub>-inert air: 45 m/sec  
velocity of stream of SO<sub>2</sub>-containing air: 55 m/sec

Table 5

	Com- parative example	Present example
temperature of film stream at a point 13 cm away from SO <sub>2</sub> -feeding nozzle (°C)	30	45
unreacted oil content (obtained through ion-exchange process) (active basis) (wt.%)	2.30	2.15
coloring (5% concentration) (absorbance: 10 mm cell, 420 mμ)	0.014	0.012

## EXAMPLE 5.

Sulfonation was effected by applying the same procedures as in Example 1 except for the following modification of the conditions. The result was as shown in Table 6.

organic material: alkyl benzene (mean molecular weight: 243)  
molar ratio of SO<sub>2</sub> (relative to organic material): 1.05  
stream of SO<sub>2</sub>-air: concentration of SO<sub>2</sub> gas = 6.1 vol.%  
stream of SO<sub>2</sub>-containing cooling gas:  
amount of SO<sub>2</sub> employed (relative to the whole amount employed): 10 wt.%  
concentration of SO<sub>2</sub> gas: 0.30 vol.%  
temperature of cooling water: 26°C  
velocity of stream of SO<sub>2</sub>-inert air: 45 m/sec

7  
velocity of stream of SO<sub>2</sub>-containing air: 49 m/sec

Table 6

	Present example
temperature of film stream at a point 13 cm away from SO <sub>2</sub> -feeding nozzle (°C)	46
unreacted oil content (petroleum ether extract) (active basis) (wt.%)	1.10
coloring (5% concentration) (absorbance : 10 mm cell, 420 mμ)	0.010
content of alcohol insoluble matter (active basis) (wt.%)	0.75

## EXAMPLE 6.

Sulfation was effected by applying the same procedures as in Example 1 except for the following modification of the conditions. The result was as shown in Table 7.

organic material: synthetic alcohol having 12 carbon atoms (mean molecular weight: 205)  
molar ratio of SO<sub>2</sub> (relative to organic material): 1.02  
stream of SO<sub>2</sub>-air: concentration of SO<sub>2</sub> gas = 7.2 vol. %  
stream of SO<sub>2</sub>-containing cooling air:  
amount of SO<sub>2</sub> employed (relative to whole amount employed): 6 wt. %  
concentration of SO<sub>2</sub> gas: 0.21 vol. %  
temperature of cooling water: 25°C  
velocity of stream of SO<sub>2</sub>-inert air: 45 m/sec  
velocity of stream of SO<sub>2</sub>-containing air: 62 m/sec

Table 7

	Present example
temperature of film stream at a point 13 cm away from SO <sub>2</sub> -feeding nozzle (°C)	48
unreacted oil content (petroleum ether extract) (active basis) (wt.%)	2.80
coloring (5% concentration) (absorbance : 10 mm cell, 420 mμ)	0.012

What is claimed is:

1. In a process for sulfonating α-olefins having 8 to 30 carbon atoms, comprising flowing a thin film of said α-olefin having a temperature of from 10° to 45°C along an externally cooled reaction surface in a reaction zone, and contacting said film with a separately supplied first stream of a mixture of gaseous sulfur trioxide and inert gas and with a separately supplied second stream of cooling gas that flows in parallel with said film and said first stream and is located therebetween, the volumetric flow rate of said second stream being

from 2 to 12 times the volumetric flow rate of the first stream, whereby to effect sulfonation, the improvement which comprises: the second gaseous stream consists essentially of a mixture of gaseous sulfur trioxide and inert gas and said second stream is flowed into the feed end of said reaction zone in parallel with, in contact with and between said film and said first stream so as to form at the feed end of said reaction zone a parallel flowing layer of said second gaseous stream between said film and said first stream, said second stream having a temperature of from 10° to 40°C and having a velocity in the range of from 1 to 1.4 times the velocity of the first stream, said second stream containing from 0.01 to 2 volume percent of sulfur trioxide and the balance is inert gas, said first stream containing from 3 to 15 volume percent of SO<sub>2</sub> and the balance is inert gas, said first stream having a velocity of from 20 to 100 m/sec and a temperature of from 20° to 50°C, said second stream supplying from 1 to 20 weight percent of the total SO<sub>2</sub> supplied by both the first and second streams.

2. In a process for sulfating condensation products of ethylene oxide with an aliphatic alcohol having 8 to 22 carbon atoms, comprising flowing a thin film of said condensation product having a temperature of from 10° to 45°C along an externally cooled reaction surface in a reaction zone, and contacting said film with a separately supplied first stream of a mixture of gaseous sulfur trioxide and inert gas and with a separately supplied second stream of cooling gas that flows in parallel with said film and said first stream and is located therebetween, the volumetric flow rate of said second stream being from 2 to 12 times the volumetric flow rate of the first stream, whereby to effect sulfation, the improvement which comprises: the second gaseous stream consists essentially of a mixture of gaseous sulfur trioxide and inert gas and said second stream is flowed into the feed end of said reaction zone in parallel with, in contact with and between said film and said first stream so as to form at the feed end of said reaction zone a parallel flowing layer of said second gaseous stream between said film and said first stream, said second stream having a temperature of from 10° to 40°C and having a velocity in the range of from 1 to 1.4 times the velocity of the first stream, said second stream containing from 0.01 to 2 volume percent of sulfur trioxide and the balance is inert gas, said first stream containing from 3 to 15 volume percent of SO<sub>2</sub> and the balance is inert gas, said first stream having a velocity of from 20 to 100 m/sec and a temperature of from 20° to 50°C, said second stream supplying from 1 to 20 weight percent of the total SO<sub>2</sub> supplied by both the first and second streams.

\* \* \* \* \*



[54] **PROCESS FOR RECOVERING ANHYDROUS ALKANESULFONIC ACIDS BY REDUCED PRESSURE, FALLING FILM EVAPORATION**

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[73] **Assignee:** Penwalt Corporation, Philadelphia, Pa.

[21] **Appl. No.:** 461,776

[22] **Filed:** Jan. 28, 1983

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[52] **U.S. Cl.:** 203/15; 203/73; 203/89; 203/72; 203/90; 203/91; 159/48.2; 159/49; 202/172; 260/513 R

[58] **Field of Search:** 260/513 R, 502 R, 400, 260/503; 203/15, 89, 14, 91, 90, 73, 72; 159/47.1, 48 L, 49, 13 R, 13 A, 13 B, 3; 202/172, 236

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

1,124,729 7/1938 Custer et al. 23/206  
2,234,166 3/1941 Hickman 202/236

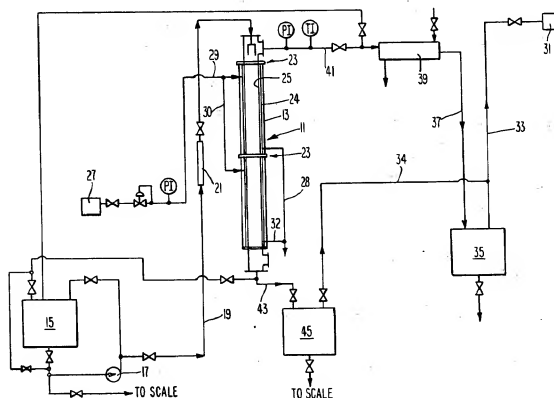
2,285,337 6/1942 Kapp et al. 203/15  
2,711,388 6/1955 Mottern et al. 203/15  
2,728,717 12/1955 Madorsky 202/173  
2,909,469 10/1959 Griffith 202/172  
3,003,930 10/1961 Pugh et al. 202/236  
3,444,049 5/1969 Starmer et al. 202/172  
3,509,206 4/1970 Nielsen 260/502 R  
3,684,459 8/1972 Tate et al. 422/138  
3,713,786 1/1973 Unstead 23/307  
3,820,582 6/1974 Rönholm 159/18  
4,035,242 7/1977 Brandt 203/15  
4,164,441 8/1979 Kühnlein et al. 159/13 A  
4,173,246 11/1979 Nuhlist et al. 159/6 W  
4,289,577 9/1981 Mabuchi et al. 159/5

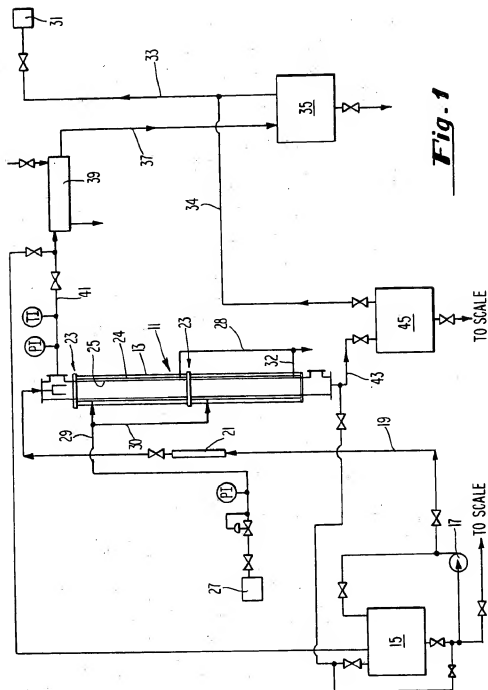
**Primary Examiner—Wilbur L. Bascomb, Jr.**

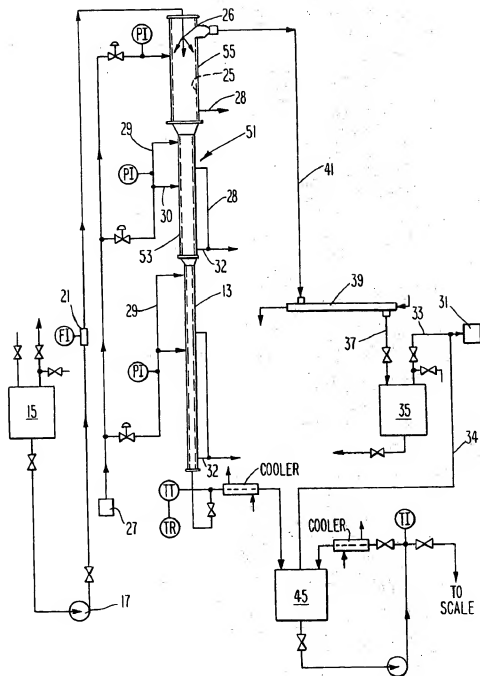
**[57] ABSTRACT**

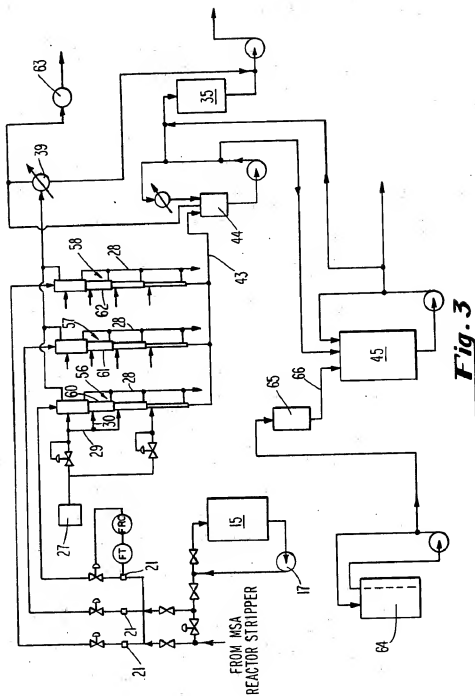
Water is removed from methanesulfonic acid to produce an anhydrous product of high purity by spraying wet methanesulfonic acid (MSA) onto the walls of a vertical, heated tube which is maintained at reduced pressure. The water evaporates as the acid flows down the walls of the tube and dry MSA is removed at the bottom.

**12 Claims, 3 Drawing Figures**





**Fig. 2**



# PROCESS FOR RECOVERING ANHYDROUS ALKANESULFONIC ACIDS BY REDUCED PRESSURE, FALLING FILM EVAPORATION

## BACKGROUND OF THE INVENTION

In the manufacture of methanesulfonic acid, an aqueous product which normally contains about 20 to 35 weight percent of water is produced. In order to obtain an anhydrous, (<2 wt. percent water) product, useful, for example, as a reaction medium in the preparation of aromatic peroxy acids where excess water retards the reaction, the water must be removed while minimizing the formation of decomposition products. Of special concern is the need to avoid the formation of methyl methanesulfonate ( $\text{CH}_3\text{SO}_2\text{OCH}_3$ ). This compound is a known carcinogen. A two-step distillative purification process for lower-alkanesulfonic acids is disclosed in U.S. Pat. No. 4,035,242. Water vapor is removed in the first step by distillation and the major portion of the alkanesulfonic acid is vaporized and removed by vacuum distillation in the second step. In the example, a product having a purity of 98.89 weight percent is obtained. Besides water, the product is reported to contain an average of 0.08 weight percent methyl methanesulfonate and 0.46 weight percent sulfuric acid. I have now found a process in which an anhydrous alkanesulfonic acid can be prepared, in a single step, without vaporizing the acid product, to a purity of at least 99.5 weight percent. The acid contains less than 1.0 ppm of methyl methanesulfonate and no detectable sulfates.

## BRIEF SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a process for reducing the water content of a lower-alkane-sulfonic acid while minimizing the formation of decomposition products. A mixture containing water and lower-alkane-sulfonic acid is placed onto the internal surface of a vertical evaporator column to form a film of the mixture on the surface. The surface is heated and the column is maintained at subatmospheric pressure so that the water evaporates as the mixture flows by gravity down the surface of the column. Water vapor is removed from the top of the column and the lower-alkanesulfonic acid, having a reduced water content, is removed from the bottom of the column.

The column can be constructed of several sections having different internal diameters to provide a progressively larger internal volume from bottom to top so as to facilitate the evaporation and removal of the larger water vapor stream in the upper portion of the column. Two or more columns can be arranged in parallel to provide increased throughput.

## DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating a system for carrying out the process of the inventions.

FIG. 2 is a schematic diagram illustrating an alternate system for carrying out the process of the invention in which the evaporation column is formed of several sections of different internal diameters.

FIG. 3 is a schematic diagram illustrating an alternate system for carrying out the process of the invention in which a series of evaporator columns are arranged in parallel.

## DETAILED DESCRIPTION

Turning now to FIG. 1, a vertically-arranged, steam-jacketed falling film evaporator column 11 is constructed of a 2-inch in diameter, 11-foot long section of jacketed, glass-lined steel pipe 13. Storage tank 15 is provided for the aqueous alkanesulfonic acid. Pump 17 is provided to feed the alkanesulfonic acid from storage tank 15 through line 19 to the top of column 11 onto a TEFLON® distributor plate 23. Rotameter 21 monitors the flow of aqueous acid to column 11. Plates 23 act to form and maintain a film of the aqueous acid on the surface 25 of inner wall 24 of pipe 13. Wall 24 is heated to temperatures of from about 300° to 375° F. by steam under pressure, or by other suitable means, fed from a supply 27, through lines 29 and 30 to the jacket portion of pipe 13. The steam leaves the jacket through lines 28 and 32. Line 41 is provided to remove water vapor and some acid which is also vaporized to a cold water condenser 39. Weak acid recovery tank 35 is used to collect the condensed water-acid mixture from line 37. Product tank 45 is provided to collect the anhydrous acid. The central core of pipe 13 is arranged to be maintained at a reduced pressure of from about 15 to 30 mm of Hg by a two-stage steam jet vacuum system 31 absolute by which is connected to the inner core of pipe 13 and also to weak acid recovery tank 35 and product tank 45 through lines 33 and 34 so as to equalize the pressure in the system.

In operation, an acid-water mixture, for example 70 weight percent methanesulfonic acid (MSA) and 30 weight percent water, at ambient temperature in storage tank 15 is fed by pump 17 through line 19 and rotameter 21 at the rate of about 17 pounds per hour to the top of column 11 where it is placed onto distributor plate 23 which forms a film of aqueous acid on surface 25 of wall 24. Wall 24 is heated by steam (10 lbs./hour) to a temperature of about 375° F. The film flows by gravity down the surface 25. The central core of pipe 13 is maintained at a reduced pressure of about 25 mm of mercury absolute so that the water is removed from the aqueous acid film efficiently without either vaporizing excessive amounts of MSA or requiring heating of the MSA to a temperature which would cause significant decomposition. The water and some vaporized MSA (overhead) leaves column 11 at the top through line 41 which carries the vapor to cold water condenser 39. The condensed liquid is removed to weak acid recovery tank 35 from which the acid-water mixture, which contains, for example, about 75% water and 25% MSA, is returned to the MSA production process. A highly purified (>99.5 wt. %), substantially anhydrous (<0.5 wt. % water), MSA product is recovered at the bottom of column 11 through line 43 and is collected in product tank 45.

FIG. 2 illustrates an apparatus for carrying out the process of the invention with an evaporator column 51 having three sections, 13, 53, and 55 of jacketed steel pipe. Section 55 is an 8-inch in diameter, 6-foot long, jacketed, glass-lined pipe, and section 53 is a 4-inch in diameter, 10-foot long, jacketed, glass lined pipe. Pipe 13 is 2 inches in diameter and 11 feet long as described in FIG. 1. A steam system is provided so that the steam is supplied at a different pressure to the jacket of each evaporator section because of the pressure rating limitations of the jacketed glass-lined pipe. For example, the following steam pressures, feed rates, and temperatures are employed:

TABLE I

Section	Rate lbs/hr	Steam PSIG	Temperature °C
Top	40	60	153°
Middle	34	125	178°
Bottom	20	175	192°

The remainder of the apparatus is similar to that illustrated in FIG. 1 and corresponding parts are designated by the same reference numerals. A spray nozzle 26 is employed to spray the aqueous MSA onto the surface 25 at the top of section 55 to form the film on the surface in place of a distributor plate.

In Tables II and III, flow rates, in pounds per 24 hour day, for a typical operation of the process using the apparatus of FIG. 2 are given, along with the weight percent recovery of product. The temperatures and pressures are given in Table III. The walls of column 51 are heated to a temperature of about 300° F. in the top section, 325°-350° F. in the center section, and about 375° in the bottom section.

TABLE II

Component	Feed lb./day	Overhead lb./day	Product lb./day	Prod./Feed Wt. % Recovery
MSA	869	123	746	86
H <sub>2</sub> O	373	369	3.8	1
Total	1242	492	750	60

TABLE III

	Feed	Overhead	Product
Wt. % MSA	70	25	99.5
Temp. °C	ambient	—	150-140°
Pressure, mm Hg. abs.	—	49	49

The product from a typical run was analyzed, and no methyl methane sulfonate could be detected (<1.0 ppm). The MSA contained at least 99.5% by wt. MSA, no detectable sulfates, and some trace impurities which were not identified. The remainder of the product was water, i.e., about 0.5 weight percent. The product was slightly darkened by the heating (APHA 500), and a small amount of 70 wt. % hydrogen peroxide was added to provide improved color (APHA 60). For example, about 12 ounces by volume of 70% aqueous H<sub>2</sub>O<sub>2</sub> per six hundred pounds of product.

Turning now to the embodiment of FIG. 3, in order to provide increased throughput, three falling film evaporator columns 56, 57 and 58 are provided which each include four glass lined, steam jacketed sections with 6-inch in diameter sections 60, 61, 62 being added between the 4 and 8 inch sections of the column 51 shown in FIG. 2. Also, instead of a steam jet vacuum source, a vacuum pump 63 is employed to reduce the pressure in the evaporator columns to about 25 mm of Hg absolute. An intermediate hold tank 44 is provided whereby off-spec product can be pumped to the weak acid recovery tank 35 for recycling to the reaction mixture. Supply 64 of 70% H<sub>2</sub>O<sub>2</sub> is provided along with metering tank 65 so that small amounts of H<sub>2</sub>O<sub>2</sub> can be added through line 66 to the product MSA order to improve the color. The remainder of the apparatus is similar to that shown in FIG. 2 and corresponding parts are shown by the same reference numerals.

Although the preferred embodiments of the process of the invention have been described with respect to the dehydration of MSA, it should be understood that the process can also be employed with water containing mixtures (5-60 percent by weight of water) of other lower-alkane sulfonic acids (i.e., 1-8 carbon atoms) such as ethanesulfonic acid by the proper selection of operating temperatures and pressures. The process provides substantially anhydrous alkanesulfonic acids, i.e., less than 0.5 weight percent water from materials containing upwards of 10% of water in a single evaporation step in which 85% by wt. or more of the acid in the feed stream is recovered in highly pure form. The product acid does not contain detectable amounts of carcinogenic byproducts.

1 claim.

1. A process for reducing the water content of a lower-alkanesulfonic acid comprising placing a mixture containing water and said lower-alkanesulfonic acid onto the internal surface of an evaporator column so as to form a falling film of said mixture on said surface, operating said column at subatmospheric pressure and heating said surface so that water is vaporized from said mixture as said film flows down said surface, removing water vapor at the top of said column, and removing lower-alkanesulfonic acid having a water content of less than 2 percent and no detectable amounts of carcinogenic decomposition products at the bottom of said column.

2. The process of claim 1 wherein said mixture contains from about 5 to 60 percent by weight of water.

3. The process of claim 1 wherein the internal surface of the evaporator column is heated to a temperature of from about 300° to 375° F.

4. The process of claim 3 wherein the internal surface of the column is heated to a higher temperature at the bottom than at the top of the column.

5. The process of claim 1 wherein the column is operated at a pressure of from about 15 to 50 mm of Hg absolute.

6. The process of claim 1 wherein the evaporator column is provided with a larger internal diameter at the top so as to provide a larger volume of water vapor in the upper portion of the column.

7. The process of claim 6 wherein the evaporator column is formed in sections having different diameters so as to provide a progressively increasing volume of water vapor from the bottom to the top of the column.

8. The process of claim 7 wherein the diameter of the water vapor stream at the top section of the evaporator is 8" and the diameter of the water vapor stream at the bottom section of the evaporator is about 2".

9. The process of claim 1 wherein portions of said mixture are fed simultaneously to a plurality of evaporator columns which are arranged in parallel.

10. The process of claim 1 wherein said mixture comprises aqueous methanesulfonic acid.

11. The process of claim 10 wherein the lower-alkane-sulfonic acid is methanesulfonic acid and the product contains at least about 99.5% by wt. of methanesulfonic acid and less and 1 ppm of methyl methane-sulfonate.

12. The process of claim 1 wherein said film is formed by spraying the mixture onto said surface.

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**United States Patent** [19]**Johnson, Jr.**[11] **4,059,620**[45] **Nov. 22, 1977****[54] PROCESS FOR PREPARING OLEFIN SULFONATES****[75] Inventor:** Fred Lowery Johnson, Jr., Austin, Tex.**[73] Assignee:** Texaco Development Corporation, New York, N.Y.**[21] Appl. No.:** 361,264**[22] Filed:** May 17, 1973**[51] Int. Cl.:** C07C 139/00**[52] U.S. Cl.:** 260/513 T; 260/456 R**[58] Field of Search:** 260/456 R, 457, 513 R, 260/513 T**[56] References Cited****U.S. PATENT DOCUMENTS**

3,328,460	6/1967	Vander Mey	260/513 R
3,350,428	10/1967	Brooks et al.	260/456 R
3,427,342	2/1969	Brooks et al.	260/457
3,441,191	5/1969	Nielsen	260/513 R
3,531,518	9/1970	Olsen et al.	260/513 R
3,769,332	10/1973	Nagayama et al.	260/513 R
3,781,339	12/1973	Tuvell et al.	260/513 R

*Primary Examiner*—Norman Morgenstern  
*Attorney, Agent, or Firm*—James L. Bailey**[57] ABSTRACT**

An improved process for preparing olefin sulfonic acids and sulfonates by the reaction of sulfur trioxide and an olefin mixture having 14 to 16 carbon atoms per molecule which includes at least 30 percent by weight dimer olefins is disclosed. The olefin mixture and sulfur trioxide are mixed and reacted in a reaction zone of a continuous falling film reactor apparatus having a segregated cooling jacket, wherein the upper  $\frac{1}{2}$  to  $\frac{3}{4}$  of the reaction zone is operated and maintained at a constant temperature of between about 0° to below about 27° C and the lower  $\frac{1}{4}$  to  $\frac{1}{2}$  of the reaction zone is operated and maintained at a higher constant temperature of between about 25° to about 40° C. The acidic reactor effluent is then aged prior to neutralization. The improved process produces a resulting product having a low oil content and low color at increased production rates while greatly reducing the off gas plume for improved air pollution abatement.

**7 Claims, No Drawings**

## PROCESS FOR PREPARING OLEFIN SULFONATES

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The invention relates to the preparation of olefin sulfonates and more particularly pertains to an improved process for producing olefin sulfonic acids and sulfonates of improved low oil content and low color from mixtures of olefins having 14 to 16 carbon atoms per molecule which contain at least 30 percent by weight dimer olefins.

#### 2. Description of the Prior Art

Processes for producing olefin sulfonic acids and olefin sulfonates by the use of continuous falling film reactor apparatus are well known in the art. Generally, conventional continuous falling film reactor apparatus comprise a vertical reaction zone surrounded by a suitable heat exchange means, and include means for forming a continuous falling thin film of olefin product in the reaction zone and a means for injecting sulfur trioxide into the reaction zone. The thin continuous falling film of the olefin to be sulfonated is formed in the reaction zone and sulfur trioxide, with a gaseous diluent, is mixed and reacted therewith. The sulfonation reaction which occurs is normally highly exothermic, depending upon the particular olefin utilized, resulting in an olefin sulfonic acid reaction product or effluent. Through the use of the heat exchange means, the exothermic reaction temperature can be substantially controlled, thereby retarding degradation of the acidic reaction product which produces off-color and other undesirable problems. Examples of prior art processes for preparing olefin sulfonates by the use of continuous falling film reactor apparatus are disclosed in the following U.S. Pat. Nos.: 3,169,142; 3,501,276; 3,420,875; and 3,461,053.

There are, of course, several variations known in the art of the above-described somewhat conventional process and apparatus for the production of olefin sulfonic acids and sulfonates. For instance, Brooks teaches in U.S. Pat. No. 3,620,684 an improved process and apparatus for continuous sulfonation of olefins wherein the acidic reaction product of an olefin and sulfur trioxide mixed and reacted in a reaction zone is immediately cooled after passing from the reaction zone, to retard degradation thereof. The preferred method of cooling disclosed is a recycle-quench step of the acidic reaction product which aids completion of the sulfonation reaction.

However, attempts heretofore to produce olefin sulfonic acids and sulfonates of low oil content and low color from olefin feed mixtures having 14 to 16 carbon atoms per molecule wherein at least 30 percent by weight of the mixtures are dimer olefins have been substantially unsuccessful, particularly at acceptable production rates. The acidic reaction products or effluent from the above-described  $C_{14}$ - $C_{16}$  dimer olefin mixtures mixed and reacted with sulfur trioxide are highly thermally sensitive. On the other hand, the sulfonic acid and sulfonate products prepared from  $C_{14}$ - $C_{16}$  dimer olefin mixtures are highly desirable for use in preparing light duty liquid detergents which are biodegradable. In the preparation of these products by prior art processes, the production rate is normally quite low and additional treatment steps are usually required to lower the oil content and off-color.

Another disadvantage in the use of known prior art processes and apparatus for preparing olefin sulfonic acids and sulfonates from the above-described  $C_{14}$ - $C_{16}$  dimer olefin mixtures is the concurrent production of off gas plumes that are most difficult to treat for air pollution abatement. Tests have shown that these off gas plumes include not only inert diluent gas and unreacted sulfur trioxide but also large amounts of the sulfonic acid reaction product in aerosol form. Hence, expensive pollution abatement devices must be utilized, e.g., alkaline scrubbing devices, after burners and the like, before the off gas plume can be released into the atmosphere.

### SUMMARY OF THE INVENTION

The present invention is an improved process for preparing olefin sulfonic acids and sulfonates by the reaction of sulfur trioxide and an olefin in the reaction zone of a continuous falling film reactor apparatus to produce an acid reaction effluent followed by aging and neutralization. The improvement of the invention comprises mixing and reacting sulfur trioxide and a mixture of olefins containing 14 to 16 carbon atoms per molecule, wherein at least 30 percent by weight of the mixture is dimer olefins, in the reaction zone of a continuous falling film reactor apparatus, operating and maintaining the upper  $\frac{1}{3}$  to  $\frac{1}{2}$  of the reaction zone at a constant temperature of between about 0° to below about 27° C, operating and maintaining the lower  $\frac{1}{3}$  to  $\frac{1}{2}$  of the reaction zone at a higher constant temperature of between about 25° to 40° C and then aging the resultant acidic reactor effluent at about 20°-45° C prior to neutralization. By the practice of the invention, the resultant acidic reaction product and/or sulfonate product, produced after conventional neutralization, have low oil content and low color, even when produced at high production rates. The resultant products are highly acceptable for use in the production of biodegradable, light-duty liquid detergents. Moreover, by the practice of the invention, the off gas plume contains greatly reduced levels of aerosol acidic product along with an improvement in product recovery.

Other objects and advantages of this invention will become readily apparent to one skilled in the art from the ensuing descriptions of the invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As mentioned hereinbefore, the instant invention is applicable for the preparation of olefin sulfonic acids and sulfonates from mixtures of olefins having 14 to 16 carbon atoms per molecule that contain at least 30 percent by weight dimer olefins. The remaining 70 percent by weight of the mixtures may be  $C_{14}$ - $C_{16}$  alpha olefins. However, it will be readily understood by those skilled in the art that the applicable olefin mixtures may contain minimal amounts of alpha, and/or dimer olefins having from 12 to 20 carbon atoms per molecule and internal olefins along with certain unknowns or impurities, e.g., below about 10 percent by weight of the olefin feed mixture.

The invention is especially applicable for the preparation of olefin sulfonic acids and sulfonates from  $C_{14}$ - $C_{16}$  olefin feed mixtures containing about 30-70 based upon the weight of the total mixture, with 50% by weight dimer being optimum. In addition, a preferred olefin feed mixture has an average molecular weight of about 196 to 224. The resulting products are highly desirable



for the preparation of biodegradable light duty liquid detergents.

In carrying out the instant invention, a continuous falling film of the above-described olefin mixture is formed in a reaction zone of a continuous falling film reactor apparatus. Sulfur trioxide is then mixed and reacted therewith in a conventional manner, such as by injection a sulfur trioxide vapor, with a diluent inert gas, into the reaction zone under pressure to increase turbulence in the falling film of olefin mixture. Procedures and apparatus for forming thin films of an olefin mixture and mixing and reacting them with sulfur trioxide in a reaction zone are well known in the art, as mentioned hereinbefore and, hence, a detailed description thereof will not be set forth.

However, in the present invention, the upper  $\frac{1}{2}$  to  $\frac{3}{4}$  of the reaction zone of the apparatus is operated and maintained at a constant temperature of between about 0° to below about 27° C while the olefin film and sulfur trioxide are mixed and reacted. Although any conventional means known in the art for maintaining a constant temperature may be used, we prefer to surround the reaction zone with a segregated cooling jacket and circulate through the upper section thereof a heat absorbing fluid, e.g., water, that will remove exothermic reaction heat from the reaction zone at an adequate rate to maintain constancy.

It has been shown that the exothermic reaction of the olefin mixture and sulfur trioxide is very rapid and approaches completion while the falling film of olefin and reaction product is within the upper  $\frac{1}{2}$  to  $\frac{3}{4}$  of the reaction zone. Accordingly, I have found that by operating and maintaining the upper  $\frac{1}{2}$  to  $\frac{3}{4}$  of the reaction at a constant temperature between 0° to below about 27° C a superior sulfonic acid product and superior sulfonate product, after neutralization, is obtained with excellent low oil content and low color characteristics, yet the rate of production can be increased greatly. Moreover, most unexpectedly there is a great reduction in off gas plume containing the sulfonic acid reaction product in aerosol form which tremendously facilitates pollution abatement.

Furthermore, experiments have shown that maintaining and operating the upper  $\frac{1}{2}$  to  $\frac{3}{4}$  of the reaction zone at the above-described temperature range is most critical. I have found that when the upper level is operated and maintained at constant temperatures either below 0° or above about 27° C, even at conventional production rates, the resulting acidic reaction effluent after neutralization contains unacceptably high levels of oil and exhibits high off-color.

The lower  $\frac{1}{4}$  to  $\frac{1}{2}$  of the reaction zone of the apparatus is then operated and maintained at a higher constant temperature of between about 25° C to 40° C by any conventional means, e.g., circulating a heat absorbing fluid through a segregated cooling jacket surrounding the reaction zone. It is most critical to operate and maintain the lower part of the reaction zone at a higher constant temperature within this range in order to accomplish the desired objectives. The viscosity of the mixture of unreacted olefin and acidic reaction product formed in the reaction zone increases proportionately as the reaction between the olefin and sulfur trioxide approaches completion. As viscosity increases the rate of film flow decreases, thereby increasing the exposure of the acidic reaction product to exothermic reaction temperatures which results in thermal degradation of the reaction product. As mentioned hereinbefore, sulfonic

acids produced from  $C_{14}$ - $C_{16}$  olefin mixtures containing at least 30 percent by weight dimer olefin are highly thermally sensitive. This thermal sensitivity increases proportionately with the amount of dimer olefin.

Moreover, experiments have shown that as the percent by weight ratio of alpha olefin in the olefin feed mixture increases, the above-described segments of the reaction zone must be operated at proportionally higher temperatures, within the stated ranges. Accordingly, as the ratio of dimer to alpha olefin in the feed mixture increases, proportionally lower temperatures within the stated ranges can be employed. The optimum temperatures to be used in the operation of each segment of the reaction zone is thus dependent upon the particular make-up of the olefin feed mixture and is best determined empirically.

Although the above-described olefin feed mixture may be fed to the reaction zone of the continuous falling film reactor apparatus at any desired temperature that will permit the formation of a continuous falling thin film of olefin in the reaction zone, a temperature of between about 20°-25° C is preferred. Optimally, the olefin feed mixture is fed to the reaction zone at room temperature. Accordingly, the temperature of the sulfur trioxide is preferably between about 30°-35° C when it is injected into the reaction zone. In a preferred embodiment of the invention, a  $C_{14}$ - $C_{16}$  olefin feed mixture containing 30 to 70 percent by weight dimer olefin is mixed and reacted with  $SO_3$  vapor in a reaction zone wherein the upper  $\frac{1}{2}$  of the reaction zone is operated and maintained at a constant temperature of between about 0°-10° C. The lower  $\frac{1}{2}$  of the reaction zone is operated and maintained at a higher constant temperature of between about 25°-30° C. The upper and lower parts of the reaction zone are maintained at the designated constant temperature ranges by the use of a segregated cooling jacket surrounding the reaction zone.

The acidic reaction effluent is then aged at a temperature of between about 20°-45° C. Preferably, the effluent is aged for about 1-10 minutes at approximately room temperature. Although the aging step may be performed by the use of any conventional means, I prefer to pass the reactor effluent from the reaction zone to a cyclone phase separator. During aging, any unreacted olefin mixture remaining in the effluent is placed in further contact with sulfur trioxide for reaction and the temperature of the acidic reaction effluent is stabilized. More importantly, the aging provides the opportunity for isomerization of certain sulfone structures in the acidic reactor effluent. Specifically, the aging time prevents formation of highly insoluble beta-hydroxy sulfonates in the final neutralized and hydrolyzed product.

The aged acidic reaction effluent is then neutralized by any conventional procedure, e.g., by mixing and reacting the effluent with a caustic solution, which produces the olefin sulfonate product. The resultant neutralized olefin sulfonate product can then be further treated by any of the processes known in the art such as by hydrolysis (saponification) to provide products ready for use.

Through the practice of the instant invention,  $C_{14}$ - $C_{16}$  olefin sulfonates containing at least 30 percent by weight dimer olefins can be produced that have below about 5.0 percent oil content (basis solids) and exhibit a Klett color below about 150 (unbleached, as determined with a Klett colorimeter with a No. 42 blue filter with a 40 mm cell on a 5% solid solution in water).

even at increased production rates up to about 23 lb/(ft<sup>2</sup>·hr) (pounds feed olefin + SO<sub>2</sub> per square foot reactor surface per hour).

As mentioned hereinbefore, any conventional continuous falling film reactor apparatus may be utilized in the practice of the invention so long as the apparatus is capable of being operated and maintained at a temperature of between about 0° to below about 27° C in the upper  $\frac{1}{3}$  of the reaction zone and at a temperature of between about 25° - 40° C at the lower  $\frac{2}{3}$  of said reaction zone. Accordingly, sulfur trioxide may be obtained from any conventional source. We prefer to utilize SO<sub>2</sub> vapor from liquid SO<sub>2</sub>, mixed with an inert gaseous diluent, e.g., air, nitrogen, carbon monoxide, carbon dioxide, sulfur dioxide and the like. The gaseous SO<sub>2</sub> is preferably utilized in a concentration from about 1.0 volume percent to 10 percent in the gas feed. Moreover, the mole ratio is preferably between about 1.05 to 1.20 (SO<sub>2</sub>:olefin).

In the following examples a continuous falling film reactor apparatus consisting of three or four sections, each with its own water cooling jacket and connected together with ball joints was utilized. The reaction zone of the apparatus was defined by a reactor tube that was 5 mm (0.197 inches) I.D., constructed of glass and had a length/diameter ratio (L/D) of 165 for three sections or 234 for four sections. An olefin reservoir near the top surrounded the reactor tube and the olefin mixture being mixed and reacted overflowed a cut in the reactor tube to flow down the reactor inner wall in a thin film. SO<sub>2</sub> vapor, from SO<sub>2</sub> originally pumped as a liquid into a heated bomb swept with dry air, emerged into the reactor tube at a point below the top of the upper water jacket where it contacted the olefin mixture film as it moved downwardly the reactor wall. Adequate turbulence in the olefin film was generated by the SO<sub>2</sub>-air stream plus a secondary air stream entering the reactor tube from above the olefin mixture feed point. Air fed through the reaction zone was dried over 3-A molecular sieves and metered by rotameters. The olefin feed mixture was pumped with a microbellows metering pump, and the liquid SO<sub>2</sub> was pumped either with a syringe pump or a Ruska pump for larger feed rates. Water was pumped through the reactor cooling jackets at 0.3 - 0.7 g.p.m. to provide the desired constant temperatures on the reactor tube wall. In all the following Examples except Example 1, the acidic reaction effluent was passed through a cyclone phase separator which was cooled to the same temperature as the lower part of the reactor. The liquid effluent was then passed through an ager (a vessel to hold the liquid for a predetermined length of time) at room temperature and thence into a caustic solution for neutralization. In Example 1, a less efficient glass cyclone was used as a phase separator and the liquid effluent was collected as acid, aged at least 10 minutes after the run, then neutralized with caustic. In all the Examples, the neutralized slurry was saponified in a pressure bottle in a 150° C oven for 1 to 1½ hours.

The saponified slurry was then analyzed for unsaponified oil by extraction with pentane, evaporation of the pentane and weighing the oil. Color was determined with a Klett colorimeter with a No. 42 blue filter and a 40 mm cell on a 5 percent solids solution in water.

Also, in the following examples production rate is defined by pounds feed (olefin + SO<sub>2</sub>) per square foot reactor wall surface per hour (lb/(ft<sup>2</sup>·hr). When the reaction zone L/D is 234, the surface is 0.198 ft<sup>2</sup>. When the reaction zone L/D is 165, surface area is 0.146 ft<sup>2</sup>.

Reactor linear velocity is defined as the velocity of the air feed through the reactor tube in ft/sec. SO<sub>2</sub> concentration is defined as the volume percent SO<sub>2</sub> in the total gas feed. Mole ratio is defined as moles SO<sub>2</sub> fed per mole olefin mixture fed. The examples are for purposes of illustration of our invention and are not intended to be limiting thereof.

#### EXAMPLES 1-2

Examples 1 and 2 set forth in the following Table I illustrate the advantage of mixing and reacting SO<sub>2</sub> and an all dimer C<sub>14</sub>-C<sub>16</sub> olefin blend in a reactor with the upper part of the reactor cooled to near 0° C and the lower part of the reactor operated and maintained at a constant temperature of near 25° C. The olefin feed in both examples consisted of 70 percent C<sub>14</sub> dimer and 30 percent C<sub>16</sub> dimer with an average molecular weight of 204.

TABLE I

	Example No. 1	Example No. 2
Production Rate (lb/(ft <sup>2</sup> ·hr)	6.4	6.4
Mole Ratio	1.15	1.16
SO <sub>2</sub> Concentration in Gas Feed (%)	12.5	12.5
Reactor Linear Velocity (ft/sec.)	125	125
Reactor L/D	234	234
Reactor Cooling Jacket Temperatures (° C) Upper $\frac{1}{3}$	1.4	51
Lower $\frac{2}{3}$	27	51
% oil (Basis Solids)	3.7	14.1
Klett Color	71	570

#### EXAMPLES 3-7

The following Table II shows the effect on oil and color of operating and maintaining the reaction zone with the top too cold (Example 3), and with the top at 0, 10, 25, and 40° C, all with the lower part of the reaction zone operated and maintained at a temperature warm enough to permit rapid flow of the acidic reaction effluent from the reaction zone (25° C). Example 4, wherein the upper  $\frac{1}{3}$  of the reaction was operated and maintained at 25° C, gave the best results on oil and color considered together. The olefin feed mixture used in Examples 3-7 consisted of 27.6 percent alpha olefin, 63.4 percent vinylidene olefin, 7.2 percent internal olefin, 1.1 percent paraffin and 0.07 percent unknown, based upon the weight of the olefin feed mixture. The carbon distribution of the feed mixture was 0.3 percent C<sub>12</sub>, 69.1 percent C<sub>14</sub> and 30.4 percent C<sub>16</sub> with an average molecular weight of 205.

TABLE II

Example No.	3	4	5	6	7
Production Rate (lb/(ft <sup>2</sup> ·hr)	9.8	9.8	9.8	9.8	9.8
Mole Ratio	1.08	1.08	1.08	1.08	1.08
SO <sub>2</sub> Concentration (%)	2.2	2.2	2.2	2.2	2.2
Linear Velocity (ft/sec)	125	125	125	125	125
Reactor L/D	165	165	165	165	165
Jacket Temp. (° C)					
Upper $\frac{1}{3}$	-10	0	10	25	40
Lower $\frac{2}{3}$	25	25	25	25	25
Oil (Basis Solids) (%)	1.5	1.6	1.8	5.1	5.2
Klett Color	144	75	88	97	96

#### EXAMPLES 8-10

In the following Table III, Examples 8-10 illustrate that lower oil content can be obtained at high production rates by the practice of the instant invention than at lower production rates using higher temperatures in the

upper part of the reaction zone. The same feed was used as in Examples 3-7.

TABLE III

Example No.	8	9	10
Production Rate (lb/Hr/hr)	23.4	15.7	9.8
Mole Ratio	1.08	1.07	1.08
SO <sub>2</sub> Concentration (%)	2.2	2.2	2.2
Linear Velocity (ft/sec)	125	125	125
Reactor L/D	165	165	165
Jacket Temp. (°C)			
upper 1/3	0	0	25
lower 2/3	25	25	25
% Oil (Basis)	4.8	3.7	3.1
Klett Color	135	82	87

## EXAMPLES 11-13

Table IV shows the off-gas plume reduction achieved by operating and maintaining the upper 1/3 of the reaction zone at a constant lower temperature and by operating and maintaining the lower 2/3 of the reaction zone at a higher constant temperature. The reduction is shown as a reduced loss of product (increased percent recovery of feeds on material balance) because no numerical data are available for the visual density of the plume. The same olefin feed mixture was used in the Examples of Table IV as in Examples 3-10.

TABLE IV

Example No.	11	12	13
Production Rate (lb/Hr/hr)	9.8	9.8	9.8
Mole Ratio	1.08	1.08	1.08
SO <sub>2</sub> Concentration (%)	2.2	2.2	2.2
Linear Velocity (ft/sec)	125	125	125
Reactor L/D	165	165	165
Jacket Temp. (°C)			
upper 1/3	0	40	40
lower 2/3	25	25	40
Loss of Product in Plume (%)	4.2	6.0	8.2
Reduction of Loss in Plume (%)	42.8	26.8	—

## EXAMPLES 14-16

The following Table VI illustrates the optimum results obtained when the upper 25% of the reaction zone is operated and maintained at a temperature within the prescribed range and the lower 75% of the reaction zone is operated and maintained at a higher constant temperature. In Examples 14 and 15, the olefin feed mixture consisted of 28% C<sub>4</sub>α, 40% C<sub>4</sub> dimer and 29% C<sub>3</sub> dimer, by weight. The olefin feed mixture of Example 16 consisted of 57% C<sub>4</sub> dimer and 42% C<sub>4</sub> dimer, by weight.

TABLE V

Example No.	14	15	16
Production Rate (lb/Hr/hr)	7.1	7.1	9.8
Mole Ratio	1.11	1.11	1.08
SO <sub>2</sub> Concentration (%)	2.0	2.0	2.2
Linear Velocity (ft/sec)	125	125	125
Reactor L/D	234	234	165
Reactor Cooling Water (°C)			
Upper 1/3	2-4	38	1-2
Lower 2/3	38	38	25-6
% Oil (Basis Solids)	2.1	4.2	4.1
Klett Color	161	182	120

A comparison of Examples 14 and 15 show that cooling the upper 25% of the reaction zone improves oil

content of the resultant product 100% even when the lower 2/3 of the reaction zone is operated and maintained at the same constant temperature. In addition, it is pointed out that the run of Example 15 produced a very dense off-gas plume containing a high level of the sulfonic acid product in aerosol form.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

## I claim:

1. In the process for preparing olefin sulfonates by the reaction of sulfur trioxide and an olefin feed mixture in a continuous falling film reactor apparatus to produce an acid reaction effluent followed by aging and neutralization to convert said effluent to an olefin sulfonate, wherein the improvement comprises:

mixing and reacting a mixture of olefins having 14 to 16 carbon atoms per molecule, at least 30 percent by weight to 70 percent by weight of said olefin mixture being dimer olefins, and sulfur trioxide in a reaction zone of a continuous falling film reactor apparatus;

operating and maintaining the upper 1/3 to 2/3 of the reaction zone at a constant temperature of between about 0° C. to below about 10° C.;

operating and maintaining the lower 2/3 to 1/3 of said reaction zone at a higher constant temperature of between about 25° C. to about 40° C.; and aging the resultant acidic reaction effluent at a temperature of about 20°-45° C. prior to neutralization.

2. The process according to claim 1, wherein the olefin mixture is 50 percent by weight dimer olefin.

3. The process according to claim 1, wherein the upper 1/3 of said reaction zone is operated and maintained at a constant temperature of between 0° C. to below about 10° C. and the lower 2/3 of said reaction zone is operated and maintained at a higher temperature of between about 25° C. to about 40° C.

4. The process according to claim 1, wherein the olefin feed mixture has an average molecular weight of between about 196 to about 224.

5. The process according to claim 1, wherein said resultant acidic reactor effluent is aged at about 20°-35° C. for about 1-10 minutes prior to neutralization.

6. The process according to claim 1, wherein said olefin mixture contains 50 percent by weight dimer olefin having an average molecular weight of between about 196 to 224, the upper 1/3 of the reaction zone is operated and maintained at a constant temperature of about 0° to 10° and the lower 2/3 of said reaction zone is operated and maintained at a higher constant temperature of about 25° to 40° C.

7. The process according to claim 1, wherein the upper 1/3 to 2/3 of the reaction zone is operated and maintained at said constant temperature and the lower 2/3 to 1/3 of the reaction zone is operated and maintained at said higher constant temperature by the use of segregated water cooling jacket surrounding said reaction zone.

interesting web  
for conceptual sketches  
preb77



US005583240A

**United States Patent** [19]  
**Asher et al.**

[11] **Patent Number:** 5,583,240  
[45] **Date of Patent:** Dec. 10, 1996

[54] **EXOTHERMIC PROCESS WITH POROUS MEANS TO CONTROL REACTION RATE AND EXOTHERMIC HEAT**

[75] **Inventors:** William J. Asher, Half Moon Bay, Calif.; Daryl L. Roberts, Winchester, Mass.; Jerry L. Jones, Menlo Park; Douglas E. Gottschlich, Mountain View, both of Calif.

[73] **Assignee:** SRI International, Menlo Park, Calif.

[21] **Appl. No.:** 205,183

[22] **Filed:** Mar. 2, 1994

**Related U.S. Application Data**

[63] **Continuation-in-part of Ser. No. 24,989, Mar. 2, 1993, abandoned.**

[51] **Int. Cl.<sup>6</sup>** ..... B01J 8/00; B01J 12/00; B01J 14/00  
[52] **U.S. Cl.** ..... 554/98; 562/74; 562/95; 562/109; 562/110; 562/123; 568/601; 585/276  
[58] **Field of Search** ..... 562/123, 74, 95, 562/109, 110, 423/659; 568/606, 613, 620, 601; 422/135, 238, 239; 504/116, 189; 424/405; 260/1; 520/1; 554/98; 585/276

**References Cited**

**U.S. PATENT DOCUMENTS**

1,685,759	9/1928	Walter	423/659
3,375,288	3/1968	De Rosset	260/669
3,840,344	10/1974	Garbo	423/450
3,844,936	13/1974	Newton	208/108
3,918,917	11/1975	Ashina	232/283
4,056,602	11/1977	Matovich	423/349
4,179,470	12/1979	Mischenko	260/580
4,187,253	2/1980	Kurtz	260/662 R
4,261,916	4/1981	Crosby	562/123
4,352,864	10/1982	Steubers	429/18
4,442,206	4/1984	Michaels	435/68
4,624,748	11/1986	Haunschild	203/29
4,786,597	11/1988	Matsen	435/41
5,384,051	1/1995	McGinness	422/239

**FOREIGN PATENT DOCUMENTS**

0432109 11/1990 European Pat. Off. .... C01G 43/00  
61-004528 5/1986 Japan ..... B01J 19/00  
2095123 7/1981 United Kingdom ..... B01F 3/04

**OTHER PUBLICATIONS**

V. Gryaznov et al., in an article entitled "Selectivity in Catalysis by Hydrogen-porous Membranes", published in Discussions of the Faraday Society, No. 72 (1982) at pp. 73-78 (no month).  
V. M. Gryaznov, in an article entitled "Hydrogen Permeable Palladium Membrane Catalysis", published in Platinum Metals Review, 1986, 30, (2), pp. 68-72 no month.  
J. N. Armor, in a review entitled "Catalysis with Permeable Inorganic Membranes", published in Applied Catalysis, 49 (1989), pp. 1-25 no month.  
K. Omata et al., in *Applied Catalysis*, vol. 52, L1-L4 (1989) no month.

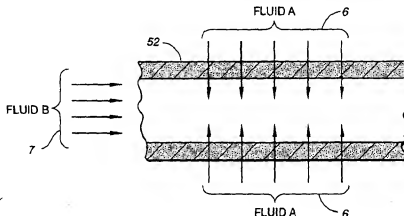
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**Attorney, Agent, or Firm**—Peters, Verny, Jones & Biksa, L.L.P.

[57] **ABSTRACT**

An exothermic process for forming a product which may be in a liquid phase is disclosed wherein a first reactant, preferably a liquid reactant, is directly fed into a reaction zone containing mixing elements and which comprises a first compartment of a reactor. A second reactant, which is maintained at a higher pressure, is fed into a second compartment of the reactor separated from the first compartment by a porous wall. The second reactant passes through this porous wall into the reaction zone to react with the first reactant. The process thereby controls rates of the reactions and the exothermic heats generated by the reactions. Pulsatile flow in one or both reaction compartments improves mixing. An evaporator for a portion of the product improves product quality and permits higher reaction temperatures in the reactor.

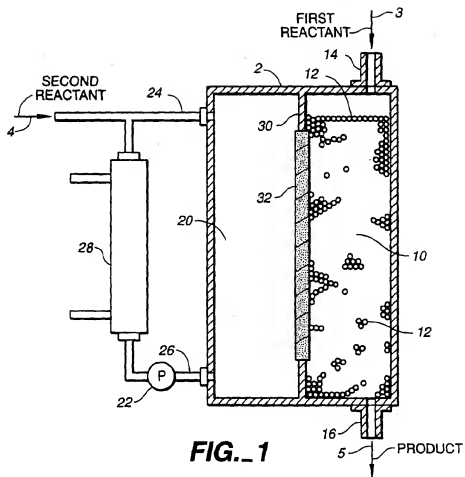
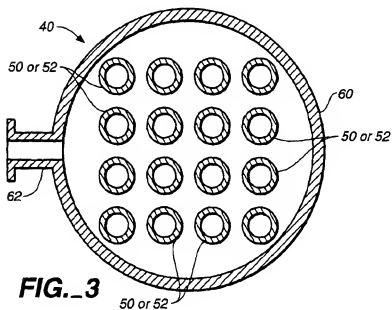
46 Claims, 6 Drawing Sheets

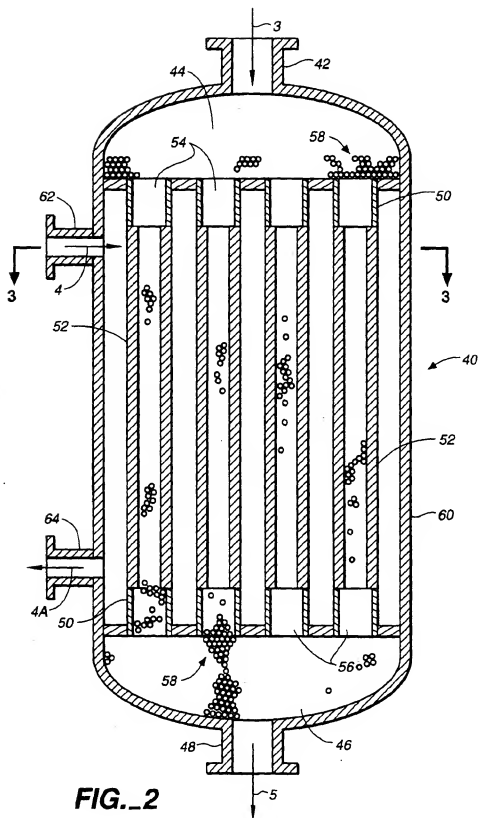


heaters  
tube-bundle reactor  
having porous tubes  
to control rxn temp  
Also included PS heat exchanger

## OTHER PUBLICATIONS

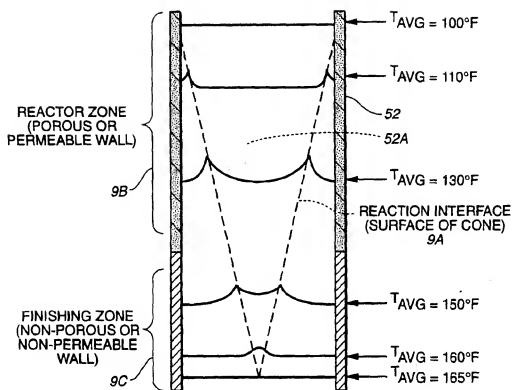
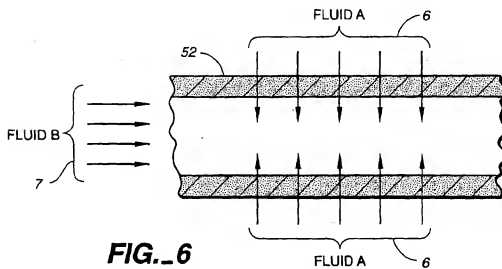
- O. Levenspiel, "Design for Multiple Reactions", Chapter 7 in *Chemical Reactions Engineering*, 2nd Ed., John Wiley and Sons, New York, New York 1983. no month.
- R. Mithail et al., in *The Chemical Engineering Journal*, vol. 23, pp. 151-160, (1982) no month.
- A. K. Barnham et al. (1983), in "High Pressure Pyrolysis of Colorado Oil Shale", Symposium on Geochemistry and Chemistry of Oil Shale, Fuel Chemistry Division, American Chemical Society Meeting, Seattle, Washington, Mar. 20-25, 1983, p. 114ff.
- K. M. Jeong et al., "Indigenous Mineral Matter Effects in Pyrolysis of Green River Oil Shale", Symposium Geochemistry and Chemistry of Oil Shale, Fuel, Geo & Petroleum Chemistry Division, American Chemical Society National Meeting, Seattle, Washington, Mar. 20-25, 1983, p. 228 ff.
- Y. T. Shah et al. *Chemical Engineering Science*, vol. 25, pp. 1947-1948, (1970) no month.
- G. Juncu et al., *Computers Chemical Engineering*, vol. 19(3), pp. 363-373, (1995) no month.
- A. Akyurtlu et al., *Computers & Chemical Engineering*, vol. 10(4), pp. 361-365, (1986) no month.
- R. De Vos et al., *Chemical Engineering Science*, vol. (12), pp. 1711-1718, (1982) no month.
- V. Hlavacek et al., *Chemical Engineering Science*, vol. 27, pp. 177-186 (1972) no month.
- R. De Vos et al., *Chemical Engineering Science*, vol. 37(12), pp. 1719-1926 (1982) no month.

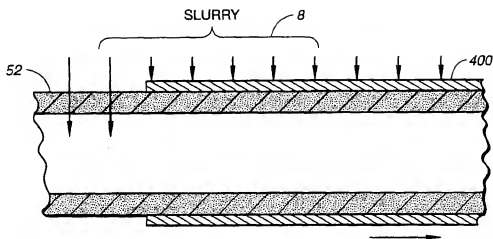
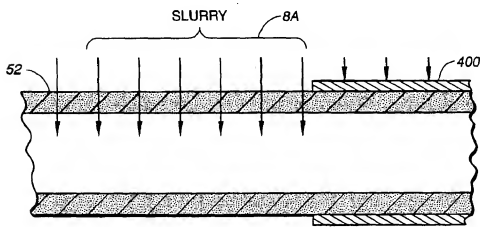
**FIG. 1****FIG. 3**

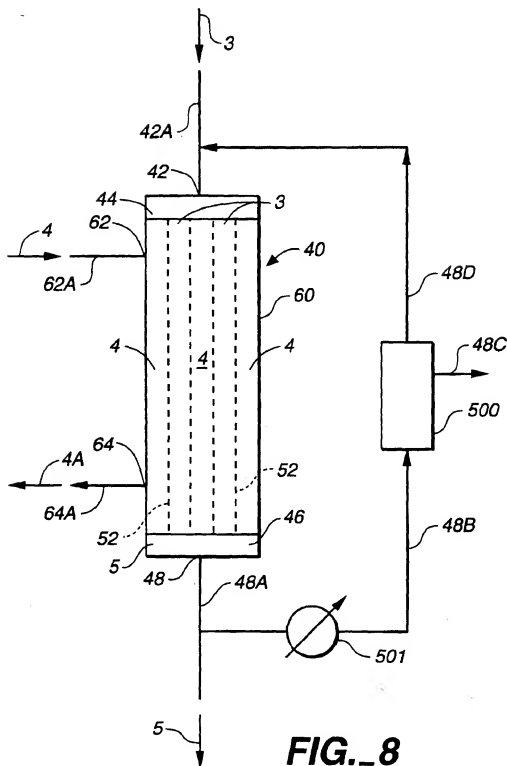
**FIG. 2**





**FIG.\_5****FIG.\_6**

**FIG. 7A****FIG. 7B**



# EXOTHERMIC PROCESS WITH POROUS MEANS TO CONTROL REACTION RATE AND EXOTHERMIC HEAT

## BACKGROUND OF THE INVENTION

### Related Applications

This application is a continuation-in-part application of U.S. Ser. No. 024,989, filed Mar. 2, 1993 now abandoned. This prior application is incorporated herein by reference in its entirety.

## FIELD OF THE INVENTION

This invention relates to a controlled exothermic process for reacting together two or more reactants. One reactant is fed at a first pressure into a first zone in a reactor containing mixing means and a second reactant is fed at a higher pressure into a second zone in the reactor. The second zone is separated from the first zone by a porous barrier wall through which the second reactant passes. In this way, a controlled flow of second reactant into the first reactor zone and control of the exothermic reaction are achieved.

## DESCRIPTION OF THE RELATED ART

Exothermic processes for forming a reaction product from at least two reactants wherein the desired product is a liquid phase or high density supercritical phase at the reaction conditions are typically carried out in a thin film reactor such as a falling film reactor. For example, Ashina et al. in U.S. Pat. No. 3,918,917 describes a multi-tube thin-film type reaction apparatus for the reaction of an organic compound and gaseous sulfur trioxide comprising a reaction tube provided with gas and liquid feeding tubes at the upper end of the reaction tube.

It is also known to carry out such reactions radially by passing reactants into a cylindrical reactor through the outer walls of the cylinder and to collect the resultant product through an apertured central tube in the cylindrical reactor.

For example, Newson in U.S. Pat. No. 3,844,936 discloses a radial desulfurization process and apparatus wherein both oil and hydrogen are peripherally introduced through sidewall nozzles into a cylindrical shell packed with catalyst. A tube having apertures therein passes through the center of the cylindrical shell, and both the oil and the hydrogen gas, passing through the catalyst in the outer shell, enter the central tube through the apertures and leave the apparatus.

De Rosset in U.S. Pat. No. 3,375,288 discloses a process and apparatus for dehydrogenation of hydrocarbons wherein a hydrocarbon feedstock to be dehydrogenated is fed into a reaction zone containing a particulate dehydrogenation catalyst. The reaction mixture, while undergoing dehydrogenation, is also contacted with one side of a tubular thin permeable membrane, such as a silver tube which has a high permeability to oxygen. Oxygen at a higher partial pressure is maintained on the opposite surface of the tube and diffuses through the tube to react with the hydrogen being liberated in the dehydrogenation process.

The use of permeable membrane catalysts, particularly the use of palladium alloy catalyst membranes, have been the subject of much investigation. Mischenko et al. in U.S. Pat. No. 4,179,470 describe a process for producing aniline by catalytic hydrogenation of nitrobenzene which comprises using a membrane catalyst which is essentially an alloy of palladium and ruthenium. The hydrogenation is carried out

by feeding nitrobenzene on one side of the membrane catalyst and hydrogen on the other side. The hydrogen reactant diffuses through the membrane catalyst, which is shaped as a foil, into the hydrogenation chamber containing the nitrobenzene reactant.

Gryaznov et al., in an article entitled "Selectivity in Catalysis by Hydrogen-porous Membranes", published in Discussions of the Faraday Society, No. 72 (1982) at pages 73-78, disclose the use of hydrogen-porous membrane catalysts through which hydrogen may pass, either during a dehydrogenation reaction to raise the reaction rate and/or suppress side reactions, or during a hydrogenation reaction to independently control to some extent the surface concentration of hydrogen and to obtain incompletely hydrogenated products which are thermodynamically unstable in the presence of hydrogen.

V. M. Gryaznov, in an article entitled "Hydrogen Permeable Palladium Membrane Catalysts", published in Platinum Metals Review, 1986, 30, (2) at pages 68-72, describes the catalytic properties of selected palladium binary alloy membranes, which are only permeable to hydrogen, during hydrogenation and dehydrogenation reactions.

Aarmor, in a review entitled "Catalysis with Permeable Inorganic Membranes", published in Applied Catalysis, 49(1989) at pages 1-25, discusses the work of others with various catalytic membranes, including hydrogen-permeable palladium membranes, ceramic-supported palladium membrane catalysts, ceramic membranes permeable to oxygen, porous polymer resins used as membranes catalysts, and alumina membrane catalysts.

K. Omasa, et al., in *Applied Catalysis*, Vol. 52, 1:1-1:4 (1989) disclose the oxidative coupling of methane using a membrane reactor. The catalyst is on the membrane or barrier, and the reactor has no mixing elements.

W. M. Haunschild in U.S. Pat. No. 4,624,748 discloses a catalyst system for use in a distillation column reaction. The entire reaction mixture passes through the permeable material. These ether-forming reactions occur at low temperatures up to about 100° C. Higher temperatures apparently would destroy the membrane.

All patent applications, patents, articles, references, standards and the like cited herein are incorporated herein by reference in their entirety.

What is needed is a process that makes it possible to control the rate of an exothermic chemical reaction by controlling the rate of contact of the one or more reactants. The present invention accomplishes these objectives of controlling exothermic reaction rate by using a porous barrier through which one or more of the reactants is introduced to the zone containing the other reactant(s), and contacting them using mixing elements.

## SUMMARY OF THE INVENTION

The present invention comprises an exothermic process for forming a product which may be in a liquid phase wherein a first reactant, or combination of first reactants, is directly fed into a reaction zone containing mixing elements and a second reactant or a combination of second reactants, which is maintained at a higher pressure, is transported through a porous barrier into the reaction zone to react with the first reactant. Preferably, the first reactant is a liquid and the second reactant is also a liquid. Control of both the reaction rate and the accompanying generation of exothermic heat are made possible by the process.

In one embodiment, the present invention relates to an improved process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

- (a) feeding into a first reactor zone one or more first reactants at a first pressure;
- (b) feeding one or more of the second reactants at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the second reactant; and
- (c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby one or more second reactants will pass through the porous wall to contact one or more first reactants in the first reactor zone and form the product.

In another embodiment, the present invention relates to an improved process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

- (a) feeding into a first reactor zone containing mixing elements therein one or more first reactants at a first pressure;
- (b) feeding one or more second reactants at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the one or more second reactants; and
- (c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby one or more second reactants will pass through the porous wall to contact one or more first reactants in the first reactor zone and form the product.

In another embodiment, the present invention relates to an improved exothermic process for forming a product by reaction of one or more first liquid reactants with one or more second liquid reactants which comprises:

- (a) feeding one or more first liquid reactants at a first pressure through a first reactor zone having mixing elements therein;
- (b) feeding one or more second liquid reactants at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by one or more second liquid reactants; and
- (c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby one or more second liquid reactants will pass through the porous wall to contact one or more first liquid reactants in the first reactor zone and form the product.

In yet another embodiment, the present invention relates to an improved exothermic process for forming a product by reaction of one or more liquid first reactants with one or more second reactants, at least one of which is gaseous at ambient conditions, which comprises:

(a) feeding one or more liquid first reactants at a first pressure through a first reactor zone having mixing elements therein;

(b) feeding one or more second reactants, at least one of which is gaseous at ambient conditions, at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the one or more second reactants; and

(c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby the one or more second reactants passes through the porous wall to contact the one or more liquid first reactants in the first reactor zone and form the product.

In still another embodiment, the present invention relates to an improved exothermic process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

- (a) feeding a first reactant at a first pressure through a first reactor zone containing mixing elements having at least one dimension equal to from about  $\frac{1}{4}$  to about  $\frac{1}{10}$  of the largest dimension of the first reactor zone normal to the flow of the first reactant through the first reactor zone;
- (b) feeding a second reactant at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the second reactant; and
- (c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby the second reactant passes through the porous wall to contact the first reactant in the first reactor zone and form the product.

In still another embodiment, the present invention relates to an improved process for forming a product by reaction of a first liquid reactant with a second liquid reactant, which process comprises:

- (a) feeding a first liquid reactant at a first pressure into a first reactor zone containing particles having at least one dimension equal to from about  $\frac{1}{4}$  to about  $\frac{1}{10}$  of the largest dimension of the first reactor zone normal to the flow of the liquid reactant through the first reactor zone;
- (b) feeding a second liquid reactant at a second pressure higher than the first pressure into a second reactor zone separated from the first reactor zone by a porous wall capable of being penetrated by the second liquid reactant; and
- (c) maintaining the pressure within the second reaction zone at all locations of the porous wall higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone;

whereby the second liquid reactant passes through the porous wall to contact the first liquid reactant in the first reactor zone and form the product.

In still another embodiment, the present invention relates to an apparatus for forming a product by reaction of one or

more first reactants with one or more second reactants, which apparatus comprises:

a reactor having one or more porous members therein dividing the reactor into first and second reactor zones capable of being maintained at different pressures; whereby the one or more first reactants in the reactor zone maintained at a higher pressure will pass through the one or more porous members into the reactor zone maintained at a lower pressure to contact one or more second reactants in the reactor zone maintained at a lower pressure to form the product.

In still another embodiment, the present invention relates to any of the improved processes described herein, wherein the process further includes step (d), (e) and (f);

- (d) conveying a portion of the reaction product of step (c) to an evaporator;
- (e) separating volatile reactants or reaction products wherein the vapor pressure of the volatile reactants or reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c); and
- (f) optionally recycling all or a portion of all of the reaction product liquid now depleted of volatile reactants, reaction products or a combination thereof to the first reactor zone of step (a).

In another aspect, the rates of flow of the first reactant in the reactor are cyclic (pulsatile) from a maximum flow rate in one direction to a rate of about a 20% reverse flow of the maximum flow rate, and return to maximum flow rate.

In another aspect, the present invention also concerns a separation, e.g. a flash evaporation, of reactants or reaction products. This separation improves the yield of the final product by reducing unwanted side reactions and reduces the formation of unwanted by-products.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a partially cutaway vertical cross-sectional view illustrating the process of the invention being carried out in its simplest form.

FIG. 2 is a schematic representation of a vertical cross-sectional diagrammatic view of an apparatus suitable for use in carrying out the process of the invention.

FIG. 3 is a top view, in cross-section of the apparatus of FIG. 2 taken along lines 3-3.

FIG. 4 is a schematic representation of a diagrammatic view of a series of stages of the apparatus generally illustrated in FIGS. 2 and 3.

FIG. 5 is a schematic representation of a graph depicting the temperature and the conical reaction interface along the flow line within a tubular reactor.

FIG. 6 is a schematic representation of a diagrammatic illustration of the respective flows of Fluid A across the walls of the porous tube and Fluid B through the tube.

FIG. 7A is a schematic representation of a cross-sectional view illustrating how the porosity of a porous tube may be varied along its length, with a shield over a portion of the porous tube.

FIG. 7B is a schematic representation of a cross-sectional view illustrating how the porosity of a porous tube may be varied along its length, with the shield shown in FIG. 7A moved to expose a further portion of the porous tube.

FIG. 8 is a schematic representation of the apparatus of the process additionally having the separator (or evaporator) component and recycle mode.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises an exothermic process for forming a chemical product which may be in a liquid

phase wherein a first reactant, preferably a liquid reactant, is directly fed into a reaction zone containing mixing elements and which comprises a first compartment of a reactor. A second reactant which may be either a liquid or gaseous reactant, and which is maintained at a higher pressure, is fed into a second compartment of the reactor separated from the first compartment by a porous wall or barrier. The second reactant passes through this porous wall into the reaction zone containing mixing elements to react with the first reactant under controlled reaction conditions.

#### Basic Apparatus Useful in the Process

Referring now to FIG. 1, the concept of the process of the invention is illustrated in its simplest form. Within a reactor 2, a first reactor compartment or zone 10 and a second reactor compartment or zone 20 are provided, separated by a wall 30 having a porous portion 32 spaced from both the top and bottom of wall 30. Reactor zone 10 is packed with mixing elements 12, such as glass balls, preferably to a level above porous portion 32 of wall 30 so as to introduce mixing into the first reactant stream 3 prior to transporting the second reactant into reactor zone 10.

A first reactant 3, which is preferably in a liquid phase, is fed through an entrance port 14 into first reactor zone 10 and a second reactant 4, which is at a higher pressure than the pressure in first reactor zone 10, is fed through entrance port 24 into second reactor zone 20. The second reactant 4 passes through porous wall portion 32 into first reactor zone 10 where it reacts to form a product 5 which is removed from first reactor zone 10 via exit port 16.

If desired, an exit port 26 is provided in second reactor compartment 20 to permit the second reactant 4 to be circulated through second reactor compartment 20, using a pump 22. As shown in FIG. 1, a heat exchanger 28 may be optionally used to cool the circulating second reactant 4 thereby remove some of the exothermic heat being generated in reactor 2.

In a preferred mode, as shown in FIGS. 2 and 3, the reaction will be carried out in a multiple tube reactor 40, having one or more tubes 50 housed in an outer shell 60 wherein a portion 52 of the wall of each tube 50 will comprise porous material. Mixing elements 58 are placed within each tube 50 and a first reactant 3, which preferably is a liquid reactant, will be fed through an inlet port 42 in the top of reactor 40 into an inlet plenum or manifold 44 connected to the open top end 54 of each tube 50. It will be noted that preferably mixing elements 58 are also placed in inlet manifold 44 so that mixing flow conditions are already created in the flow of first reactant in reactor 40 before the first reactant reaches tubes 50 and, therefore, before introduction of the second reactant 4 into the flow stream.

While 16 such tubes are illustrated in the reactor shown in FIGS. 2 and 3, it will be understood that this is for illustrative purposes only and a commercial embodiment for practicing the process of the invention would utilize a large number of such tubes, e.g., as many as 50 or more such porous tubes.

The second reactant 4 is introduced through a first side port 62 in shell 60 of reactor 40 at a higher pressure than the first reactant to circulate around all of the outside surfaces of tubes 50, including the porous portions 52 through which the second reactant is transported to contact and react with the first reactant 3 within tubes 50.

The resultant product 5, as well as any unreacted reactants, may then exit via open bottom ends 56 of each tube 50 into a second plenum or manifold 46 which, it will be noted, also contains mixing elements 58. This positioning of mix-

*can use an indirect exothermic instead*

ing elements 58 along the entire length of each tube 50, even beyond the porous portion of each tube 50 and into lower manifold 46, is provided because there may be continued reaction between the first reactant 3 and second reactant 4 even after the flow of product 5 and reactants (3 and 4) passes beyond the porous portion of each tube 50. That is, the reaction zone may extend beyond the end of the porous portion of each tube 50.

The product 5, as well as any unreacted reactants, may leave reactor 40 via exit port 48 at the bottom of reactor 40. An exit port 64 in shell 60 of reactor 40 is also provided for the second reactant 4 to permit circulation thereof, as well as possible additional use of the second reactant as a coolant for reactor 40, as discussed above.

FIG. 5 is a schematic representation of a graph which depicts the change in temperature and the conical reaction interface 9A along the flow line within a porous tubular reactor, e.g. 52, having a reactor zone 9B. Within tube 52 is found a radial reaction zone 52A surrounded by a porous wall through which the second reactant 4 passes to react with the first reactant 3. The finishing zone 9C is not porous. The average temperatures are shown at various points in the tube. The graph illustrates that the temperature within the reactor gradually rises with no hot spots in the reactor, e.g. 40.

The porous barrier 52 may or may not have catalytic properties. Preferably the barrier or wall does not have catalytic properties.

#### Mixing Elements Used in Process

The presence of mixing elements 58 in the reaction zone provide a more thorough mixing of the reactants in the reaction zone to prevent or inhibit the occurrence of hot spots in the reaction zone which could result in creation or concentration of excessive heat which could damage either reactants or product. The mixing elements preferably comprise inert materials such as glass or ceramic balls or other non-reactive packing type material such as Raschig rings or beryl saddles. In some embodiments, the mixing elements are stationary. In other embodiments, the mixing elements are mobile within the reaction zone. In one embodiment, the mixing elements do not have catalytic properties.

It is also within the scope of the invention, in another embodiment, for the mixing elements to have catalytic properties as well, although it will be appreciated that the main purpose of the mixing elements is to create multiple divisions and recombining of flow and thus provide for more thorough mixing of the reactants in the reaction zone in the reactor.

Thus, particulate catalysts conventionally utilized usually comprise finely divided materials characterized by high surface areas and short diffusion distances to maximize the contact area between catalyst and reactants, at the expense of high pressure drops, resulting in lower throughput or the need to utilize more energy in passing the reactants through such a catalyst bed.

In contrast, the mixing elements utilized in the process of the invention are much larger in size than conventional catalysts so that any negative impact on flow rates by the presence of such mixing elements will not be significant.

Preferably the mixing elements utilized in the process of the invention have a major dimension which ranges from about  $\frac{1}{16}$  inch to about  $\frac{1}{4}$  inch, preferably from about  $\frac{1}{16}$  inch to about  $\frac{1}{8}$  inch, of the largest dimension in the plane of the reaction zone normal to the flow of the reactants through the reaction zone. For example, when the mixing elements comprise balls and the reaction zone comprises a cylindrical tube, the balls will have a diameter of from about  $\frac{1}{16}$  inch to about  $\frac{1}{4}$  inch, preferably

from about  $\frac{1}{16}$  inch to about  $\frac{1}{4}$  inch, of the diameter of the tube. Thus, if the reaction zones are located within 2 cm I.D. tubes having porous tube walls, spherical mixing elements utilized within the tubes will have diameters ranging from about 0.2 millimeters (mm) to 10 mm, and preferably will range from about 2 mm to 6.7 mm.

It should be further noted that while the presence of the mixing elements has been illustrated in the reaction zone, as well as in the region just prior to the mixing zone, the mixing elements may also be reset in the conduits leading from the reactor to heat exchangers, and may even be used in the heat exchanger tubes as well. This is particularly true where the reaction zone, comprising the porous portion of a tube and the region of the tube beyond the porous region, is joined to a heat exchanger forming an extension of the same tube, in which case the entire tube is advantageously packed with such mixing elements.

The above configuration makes maximum uses of the tube volume. However, for many chemistries, the concern about the effects of possible leakage between the shell side fluids, the second reactant, and the cooling water would preclude its use. For example, in the case of sulfonating an organic compound, the second reactant 4 is  $\text{SO}_3$ , which would be separated from the cooling water by a tube sheet. A pin hole would produce hot sulfuric acid which would soon enlarge the pin hole. In these cases, separate reactors and heat exchanges would be preferred.

#### Porous Material Used In the Process

The porous material initially separating the two reactants, and through which the second reactant passes, will generally comprise a material of controlled porosity, as opposed to a pore-free permeable membrane through which transport is by diffusion, since such pore-free membranes provide poor rate performance due to the low transport rate across the membrane. The porosity and pressure are adjusted to provide a minimum flow of the second reactant across the porous material, relative to the flow of the first reactant on the low pressure side of the porous material (32 and/or 52), sufficient to permit reaction of the first reactant on the low pressure side with the second reactant passing through the porous material.

However, the flow rate of the second reactant 4 across the porous material, i.e., the porosity and pressure used, must be adjusted to not exceed that flow rate which will provide either reaction between the reactants or dissolving of the second reactant 4 into the first reactant 3 on the low pressure side, i.e., a second phase (comprising the high pressure second reactant) should not be substantially formed in the reaction zone. By "substantially" is meant that not more than 10% of the high pressure second reactant passing through the porous material (32 and/or 52) should form a second phase in the reaction zone.

Typically, the porous material will comprise a sintered metal. The porous material may comprise a high porosity (coarse) material which has been coated with a second material to control the pore size. For example, a porous stainless steel material may be coated with a non-reactive ceramic material such as zirconia. This, for example, could be done by coating a commercially produced sintered stainless steel tube with finely divided zirconia or titania powder dispersed in a vehicle, allowing the vehicle to evaporate, and then firing the zirconia (or titania)-coated tube at a temperature of 1000° C.

The coating of the commercially produced porous tube may be carried out by pumping a slurry or suspension of the coating materials, e.g., zirconia or titania, through the walls

of the porous tube, i.e., from the outside of the tube to the inside—or vice versa—until one achieved the desired porosity. When the coating or changing of the porosity is done by pumping a slurry from the outside to the inside of the porous tube, the need for heating to stabilize the porosity of the tube can sometimes be eliminated.

In one embodiment of such modification of an existing porosity of porous tube 52, it may be advantageous to provide a variable or provided porosity in porous tube 52. Referring to the graph of FIG. 6, the pressure of Fluid B (aka 7) flows inside porous tube 50 gradually drops as Fluid B (7) flows within tube 52. This, in turn, means that the change in pressure  $\Delta P$ , across the porous wall of tube 52 increases along the tube in the direction of flow of Fluid B (7) (assuming that Fluid A (aka 6) has a constant pressure all along the length of tube 50 and/or 52).

To compensate for this variable pressure drop across the wall of tube 52, there should be a continually decreasing porosity in the porous wall of tube 52. One way of achieving this, as shown in FIGS. 7A and 7B, is to cover either the inside or outside surface of porous tube 52 with a sleeve 400 which is slowly moved or retracted as the slurry 8 or suspension of the coating materials, e.g., zirconia or titania, is pumped through the walls of the porous tube. By varying the amount of material pumped through the porous walls of the tube along the length of the tube in this manner, a profiled change in the porosity of the tube may be achieved, with the portion of the tube 8A exposed the longest to the coating materials having the lowest porosity and, therefore, being located on the downstream end of the flow of Fluid B (or 7) through the tube.

The porosity of a porous metal substrate, such as a commercially available porous stainless steel tube, could also be modified by coating the porous tube with fine metal particles, and then sintering the coated tube at a temperature sufficiently low to permit the particles to sinter to the porous substrate without fusing the porous substrate into a non-porous mass. Examples of metal powders which may be used, for example, with a porous stainless steel tube include stainless steel, nickel, and chromium.

The porosity of the porous surface separating the first 3 and second reactants 4 will be selected to provide a volumetric flow rate of second reactant through the porous barrier which will result in the desired rate of reaction between the reactants. If the exothermic heat given off during the reaction is high, in accordance with the process of the invention, the reaction may be slowed by lowering the flow of the second reactant into the reaction zone. This may be accomplished, in accordance with the present invention, by selecting a barrier material having a lower porosity.

The viscosity of the reactant which is flowing through the porous barrier, as well as the pressure difference between the two sides of the porous barrier and the area of the porous barrier, also must be taken into account when attempting to adjust the volumetric flow of the second reactant across the porous barrier to thereby exercise control of the generation of exothermic heat in the reaction zone. This viscosity, if desired, may be further controlled or adjusted by blending product with the particular reactant before feeding the reactant into the reaction zone.

When these parameters are all taken into account, the porosity of a porous barrier of given area to a reactant of given viscosity at a given pressure differential across the barrier to achieve a particular volumetric flow rate may be expressed in the following equation:

$$V = \frac{Q \cdot A \cdot \Delta P}{\mu}$$

wherein:

V=volumetric flow rate of the reactant going through the porous barrier, in cubic centimeters per second (cc/sec);  
A=the outside area of the porous barrier in square centimeters (cm<sup>2</sup>);

$\mu$ =the viscosity of the second reactant passing through the porous barrier in centipoise (cp);

$\Delta P$ =the change or difference in pressure from one side of the porous barrier to the other side in pounds per square inch (psi); and

Q=the viscosity normalized permeance of the porous barrier material in cm<sup>3</sup> cp/cm<sup>2</sup> sec psi (where 1 pound per square inch (psi) is equal to 6894.7 pascal).

It will, of course, be recognized that this "viscosity normalized permeance" of a given material will vary with the porosity of the material, the wall thickness of the porous barrier, and the wall morphology, since the porosity may not be uniform. In accordance with the invention, the Q value of the porous barrier initially used to separate the first and second reactants should range from about  $10^{-4}$  to about  $5 \times 10^{-2}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi, preferably from about  $10^{-4}$  to about  $10^{-3}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi, and most preferably from about  $5 \times 10^{-4}$  to about  $5 \times 10^{-3}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi, to provide the desired initial separation while still permitting adequate permeance of the second reactant through the barrier to permit the reaction to proceed. The mean pore diameter of the pores in the barrier, depending upon its application, may generally range from between about 0.01 and 50 micrometer.

The temperature range maintained in the reactor 40 may range from the lowest temperature at which the particular second reactant 4 will still pass through the porous material, and at which both reactants (3 and 4) will be in either the gaseous or liquid states, i.e., will not become solidified. Apart from this, the low end of the temperature range maintained within the reactor will usually depend upon the desired process economics since some reactions will be unacceptably slow if the temperature is maintained too low.

The upper end of the temperature range maintained within the reactor will usually be from about 5° C. to about 200° C. below that temperature at which significant product degradation or undesirable side product formation occurs. By "significant" is meant 10% or more of the product degrades or 10% or more of the reaction product comprises the product of a side reaction.

Usually the temperature within the reactor will be within a range of from about -50° C. to about 500° C. (depending upon the particular reactants), preferably from about 0° C. to about 400° C. (again depending upon the particular reactants) and more preferably between about 110° and 400° C. (depending upon the particular reactants). For example, the reactor will be maintained within a range of from about 100° C. to about 200° C. for an ethoxylation reaction, while for a typical sulfonation process, the reactor temperature maintained within a range of from about -20° C. to about +100° C.

The outlet pressure of the reactor may be maintained at any conventional pressure used in state of the art reactors consistent with the minimum pressure needed to obtain sufficient desired product flow up to the maximum pressure which may be handled by downstream equipment, e.g., a high pressure needed to couple with downstream processing.

Inlet pressures of the reactants must be consistent with the desired outlet pressure and the pressure drop within the



reactor. The differential in inlet pressure between the first and second reactants will be a function of the permeability of the second reactant—which will, in turn, be dependent upon the physical properties of the second reactant and the porosity of the porous material in the apparatus.

It should be noted that the pressure within the second reaction zone at all locations of the porous wall should be maintained higher than the pressure in the first reaction zone at corresponding locations of the porous wall, to thereby inhibit any flow through the porous wall from the first reaction zone to the second reaction zone.

#### Reactions and Reactants Used in the Process

There are many exothermic reactions which benefit from the application of this invention. By way of examples of reactions which may be carried out using the process and apparatus of the invention, and not by way of limitation, there may be mentioned oxidations, halogenations, sulfonations, sulfations, nitrations, ethoxylation, hydrogenations, polymerizations and the like. State of the art conditions for these reactions, therefore, extend over very broad ranges of temperature and pressure.

To practice the present invention with these exothermic conditions, one of skill in the art should select the conditions for the reaction first zone to be quite near those conditions used with state of the art reactors for the reactions considered. The advantage of using the present invention is less local temperature excursions within the reactor, and better control of the transport of reactants and products throughout the reaction zone and process yielding higher quality, and more uniform reaction products.

The respective flow rates of the reactants into the reactor will, of course, depend upon a number of parameters including those just discussed, as well as the overall size of the reactor. The relative rates of reactant flow, i.e., with respect to one another, will depend upon the particular reaction, including the amount of heat generated, as well as whether or not the process will be carried out in one or more stages.

It may be desirable, when the process is conducted in a single stage apparatus, to circulate some of the product stream back to the inlet side of either or both reactants in some instances to thereby provide a further control of the reaction rate or to alter the viscosity of one of the incoming reactant flows. In the case of the first reactant 3, such dilution will result in less reactant present per given mass and heat capacity of this total flow going into the zone 1 of the reactor. Thus, the total exothermic heat of the reactions of all of this first reactant mixture 3 will result in a lower final temperature because of the larger heat capacity. Addition of the product to the second reactant stream 4 will (in many cases) serve to increase the viscosity of the second reactant stream passing through the porous barrier, thus decreasing the volumetric flow rate of second reactant passing through the porous barrier (in accordance with the previous equation) which will also serve to slow down the reaction and reduce the generation of exothermic heat.

Multiple Stage Apparatus for Conducting the Process

The preferred mode of operating the process of the invention will be in a plurality of stages, using, for example, in each stage, a shell and tube reactor such as previously described and illustrated in FIGS. 2 and 3, together with optional recirculation of product, optional addition of makeup reactants, and optional use of heat exchangers to control the overall temperature buildup as needed.

Such apparatus is illustrated in block diagram form in FIG. 4 which illustrates three stages of operation of the process of the invention. The first reactant from source 70 travels via conduit 72 through valve 74 and pump 76 to an

optional mixer 78 where the first reactant stream 3 may be optionally blended with a portion of the product stream from first reactor 100. The first reactant 3 then travels via conduit 79 into first reactor 100, which may be a shell and tube reactor similar to reactor 40 previously depicted in FIGS. 2 and 3. In this case, conduit 79 would be connected to inlet manifold 44 (FIG. 2) within reactor 100 so that the first reactant 3 flows through the tubes containing mixing elements within reactor 100 connected to inlet manifold 44.

The second reactant 4, from second reactant source 80, passes via conduit 82 through valve 83 and then through conduit 84 to optional blender 89 and then through conduit 85 to enter the shell portion of first reactor 100. As previously described with respect to FIGS. 2 and 3, the second reactant 4 then passes from the shell through the porous portions of the tubes within reactor 100 to react with the first reactant 3 flowing through the tubes.

The resulting product 5, as well as any unreacted reactant(s), leave first reactor 100 via conduit 86, where the product stream splits into two streams. Conduit 87a optionally returns some of the product stream through valve 88a to optional blender 89 where it is blended with the second reactant stream and is then fed via conduit 85 into reactor 100. The remainder of the product stream passes through conduit 87b to valve 88b and then through heat exchanger 81 and conduit 90. Conduit 90 then also splits into two portions. Conduit 92 passes a portion of the product stream to the next stage, and conduit 94 through which one may optionally recirculate product 5 back to reactor 100.

The portion of the product stream optionally recycled back to reactor 100 through conduit 94 passes through a valve 95 (which controls the ratio of product stream being recycled back to reactor 100) to pump 96 which is connected to mixer 78 via conduit 98.

By shutting off both valves 88a and 95, all of the product stream will be passed on to the subsequent stage of the apparatus, shutting off only one of valves 88a or 95 will respectively recycle the product stream back to only one of the initial reactant streams as desired.

Similarly, the relative flows of the first and second reactants into reactor 100 may be controlled by adjustment of valves 74 and 83, as well as valve 88b, either by itself (when valve 88a is shut off) or in conjunction with valve 88a, to control the flow rate through reactor 100.

The portion of the product stream to be passed on to the next stage via line 92 passes through pump 176 to optional mixer 178 where it is optionally blended with recycled product from the second stage as well as with an optional flow of further first reactant from first reactant source 70 via line 172 and valve 174, which controls the amount of fresh first reactant to be blended with the product stream from reactor 100.

The product stream from reactor 100, with or without further amounts of fresh first reactant and recycled product from the second stage, is fed into second reactor 200 via line 179. As previously described with respect to reactor 100, second reactor 200 would preferably be constructed similarly to reactor 40 illustrated in FIGS. 2 and 3, so the incoming stream from line 179 would pass into the interior of the porous tubes of the reactor via the inlet manifold.

Optional additional second reactant would then flow, via line 182 and valve 183 from second reactant source 80 to an optional blender 189 from which it would flow via conduit 185 to the shell side of reactor 200.

The product stream, emerging from reactor 200 via conduit 186, is split into two streams (as in the first stage). One stream which will flow via conduit 187a through valve 188a

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to optional blender 189 where it can be blended with fresh second reactant. The other stream will flow via conduit 187b to valve 188b and heat exchanger 181. The stream then flows via conduit 190 to a point where it again may be split between two streams to either pass on to the third stage via conduit 192 or to recirculate via conduit 194 and valve 195 back through pump 196 and conduit 198 to optional blender 178 where the product stream may be blended with fresh first reactant 3.

Similarly, in the third stage, the product stream in conduit 192 may be pumped through pump 276 to optional blender 278 where it may be optionally blended with fresh first reactant 3 entering blender 278 from source 70 via conduit 272 and valve 274, as well as with recycled product from reactor 300, as will be described below, before entering reactor 300 via conduit 279. Reactor 300 is also preferably be constructed in accordance with the previously described construction with respect to FIGS. 2 and 3. Thus, the incoming stream via conduit 279 enters the inlet manifold to be distributed to the porous tubes within reactor 300.

Optional additional second reactant 4 would then flow, via line 282 and valve 283 from second reactant source 80 to optional blender 289 from which it would flow via conduit 285 to the shell side of reactor 300.

The product stream, emerging from reactor 300 via conduit 286, is then split into two streams (as in the first and second stages). One stream which will flow via conduit 287a through valve 288a to optional blender 289 where it can be blended with fresh second reactant 4. The other stream will flow via conduit 287b to valve 288b and heat exchanger 281. It then flows by way of conduit 290 to a point where it again may be split between two streams to either pass on to the product collection point 350 via conduit 292 or to recirculate via conduit 294 and valve 295 back through pump 296 and conduit 298 to optional blender 278 where the product stream may be again blended with fresh first reactant 3.

It should be noted that while the above description of a multiple stage apparatus includes descriptions of valves and conduits which make possible the recycling of portions of the product flow back to each reactor stage and which also make possible the blending of fresh first or second reactants at every stage, these options will rarely all be exercised simultaneously. Thus, it may be possible that no product will be recycled and no fresh first or second reactants added, with the subsequent stages merely acting as an extension of the reaction zone of the first stage. Alternatively, when stoichiometric equivalents of both reactants have been initially fed into the first stage, only the recycling of product may be carried out, without any additional amounts of either reactant added to the streams entering the subsequent stages of the apparatus. Finally, if a stoichiometric excess of one of the reactants is initially fed into the first stage, only significant amounts of the other reactant may be blended with the inlet streams to subsequent stages. However, even in such circumstances, it may be necessary to add to subsequent stages minor increments of even the reactant initially added in stoichiometric excess to the first stage.

As shown in the dotted lines in FIG. 4, connected respectively to reactors 100, 200, and 300, optional heat exchanger loops, each comprising a heat exchanger 316, and a pump 320, may be connected to one or more of the reactors to remove exothermic heat generated in any or all of the reactors as needed.

In the sulfonation of the methyl laurate (or other alkyl long chain esters), the sulfur trioxide to methyl laurate feed rate is between about 0.8 and 1.2 (preferably 1.05). The sulfonation reactor outlet temperature is between about 60°

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and 100° C. (preferably about 74°–75° C.). The sulfonation pressure of the inlet is between about 250 and 350 psia (1.7x10<sup>5</sup> and 2.4x10<sup>5</sup> pascal) preferably about 300–306 psia (about 2.1 and 10<sup>6</sup> pascal). The outlet pressure is between about 50 and 100 psia (3.4x10<sup>4</sup> and 6.9x10<sup>4</sup> pascal), preferably about 65 psia (4.4x10<sup>4</sup> pascal). The residence time in the reactor is between about 1 and 4 sec. (preferably about 2.3 sec.). The conversion of methyl laurate is high, generally between about 90–99% (usually about 97–98%). The selectivity to produce alpha-sulfomethyl laurate is high, generally between about 90 and 99% (usually about 95–96%).

In one embodiment, a reactor of the present invention has an overall shell size of about 40–60 in (100–150 cm) in length, preferably about 45 in (114 cm), and a diameter of about 15–25 in (38–63 cm), preferably 19–20 in (48–51 cm). The number of porous tubes is between about 150 and 220 (preferably about 189–190). The porous tubes have between about 0.6–2.54 cm inside diameter (I.D.) (preferably about 1.6 cm) and an outside diameter (O.D.) of between about 1.27 and 3.8 cm, preferably about 2.2 cm. The reactor has between about 75 and 125 cm of active length, preferably about 100 cm. The mixing elements and mixing balls having a diameter of between about 0.5 and 0.1 cm, preferably about 0.25 cm.

#### Pulsatile Flow

In one embodiment referring to FIGS. 1 and 3, the exothermic reactor process uses, with the first reactant 3, a slurry of a catalyst 12A in reactor 10. The flow of catalyst slurry 12A with the mixing elements 12 occurs such that the flow rate of the first reactant 3 changes as a function of time. This flow rate change may be referred to as pulsatile (or pulsed) flow e.g. a sine wave, square wave, irregular wave, etc. The pulsed flow prevents the accumulation of solid catalyst particles 12A at fixed points on the mixing elements 12. This accumulation of catalyst particles 12A is not desired because it changes the flow characteristics in mixing in the reaction zone and may ultimately block the flow of catalyst or reactant or both.

Preferably, the pulsed flow changes with time in a cyclic manner. For instance, the rate of flow of catalyst slurry may change in the cycle from maximum flow to a level of about 80% of the maximum rate of flow. Preferably, the rate of flow of catalyst slurry cycles down to a level of about 50% of the maximum rate of flow of the catalyst slurry, then returns to the maximum flow rate. Preferably, the rate of flow of catalyst slurry cycles down to a level of about 20% in the reverse direction of the maximum rate of flow of the catalyst 12A, then returns to about the maximum flow rate in the original direction of flow.

In the pulsed flow, a typical example is the reaction of hydrogen with an alkene using a flowing slurry of Raney nickel catalyst particles suspended in the alkane. The maximum rate of flow of the reactant suspended catalyst corresponds to residence times of between about 0.5 to 6000 sec. The flow rate can change to achieve a rate of flow of between about 80% and ~20% ml/sec. of maximum. After remaining at this reduced flow rate (about 50% of maximum) for between about 0.1 and 1000 sec, the rate of flow is increased back to the maximum flow rate.

#### Separation (e.g., Evaporation) of Reaction Products

In one embodiment, the present invention is improved by removal of volatile reaction products. The volatile reaction products or reactants are those having a vapor pressure of about 1 mm of Hg or higher at the reaction temperature of the reaction of step (c). Referring now to FIGS. 2 and 8, reactor 40 is one having a shell 60 and having multi tube porous barrier reactors 50. The second reactant 4 enters

through inlet 62 via line 62A and is forced under pressure from the shell side through the porous barrier 52 into a recirculation stream of product 48A. The second reactant can be removed or recycled via line 64A at outlet 64. The first reactant is introduced to the reactor 60 via inlet 42 via line 42A in a continuous (or a pulsed) stream in the tube side of the reactor. A recycle loop of lines 48A and 48B, evaporator 500, and line 48D has a flash evaporator 500 to remove the volatile products of the reaction. The reaction products (or multiple components) is conveyed from outlet 48 via line 48A and 48B to an optional cooler 501 and then as a liquid via line 48B to the evaporator 500. The volatile reaction products are removed as a vapor via line 48C. The liquid product is conveyed via line 48D to line 42A, and then is recycled through the primary reactor 40. In effect, a steady state loop is created for maximum heat removal. The volatile reaction products are removed which prevents their further reaction and the formation of undesirable side products, and usually permits the operation of the primary reactor at higher temperatures, as compared to the system which does not have the evaporator, e.g. from about 520° C. up to about 200° C. higher than the reaction systems not having the evaporator.

The fields of use for the present invention include, but are not limited to, formation of a pesticide, a fungicide, a rodenticide, an insecticide, a herbicide, a pharmaceutical, a surfactant, a demulsifying agent, a fabric treatment agent, a hydrocarbon solvent, a hydrocarbon fuel, an organic polymer, a synthetic lubricant, a halogenated hydrocarbon, a fire retardant and the like.

Surfactants which are prepared according to the present invention, include but are not limited to, alkyl benzene sulfonates, linear alkylbenzene sulfonates, secondary alkane sulfonates, alpha olefin sulfonates, alkyl glyceryl ether sulfonates, methyl ester sulfonates, natural fat sulfonates, alcohol sulfates, alcohol ether sulfates and the like.

The following examples serve to further explain and describe the present invention. They are not to be construed to be limiting in any way.

#### EXAMPLE I

##### Ester Sulfonation (SO<sub>3</sub> High Flow Rate)

(a) Fresh methyl laurate, having a viscosity of 2 cp, may be fed at a rate of 550 grams/sec into a mixer where it is mixed with a 5650 grams/sec flow of recycled product and the resulting mixture is fed, at a temperature of about 38° C. (-100° F.) and a pressure of about 340 psia ( $2.3 \times 10^6$  pascal (where 1 psia=6894.7 pascal)) into the top of 85 porous wall tubes arranged vertically in a bundle in a cylindrical reactor having an inside diameter (ID) of about 20 in. (50.8 cm) Each tube has an ID of about  $\frac{3}{8}$ " (1.91 cm), and has a 110 cm. length of porous metal comprising stain-less steel fabricated by powder metallurgy to have a nominal pore size of generally about 0.2 microns (micrometers) and a viscosity normalized permeance of about  $0.0037 \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .

The tubes are each packed with inert glass balls, each having a diameter of 0.320 cm., up to a distance of 10 cm. above the porous portion of each tube and also extending to the bottom of each tube, i.e., beyond the porous portion of the tube in the direction of reactant flow.

On the shell side of the reactor, 205 grams/second of liquid SO<sub>3</sub> may be mixed with a 760 grams/sec flow of recycled product at a temperature of about 38° C. (-100° F.) and a pressure of about 350 psia ( $2.4 \times 10^6$  pascal), and fed

into the shell portion of the reactor to pass through the porous tubes and react with the methyl laurate therein.

The resulting product stream, leaving the reactor at a temperature of about 74° C. (-165° F.) and a pressure of about 65 psia ( $4.5 \times 10^5$  pascal), is fed through a heat exchanger containing 1350 tubes having an ID of 1.91 cm and 240 cm in length, and also packed with 0.32 cm diameter inert glass balls.

The sulfonated methyl laurate product from such a reactor system will be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology. This is because there is no temperature peak typical of the entry region of a falling film reactor and because there is even distribution of reactant all along the reactor length in the process of the invention.

(b) Similarly, the reaction described in Example I (a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene, the corresponding linear alkylbenzenesulfonic acid is obtained. These are useful as surfactants.

(c) Similarly, the reaction described in Example I (a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, and the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

#### EXAMPLE II

##### Ester Sulfonation (SO<sub>3</sub> Lower Flow Rate)

(a) Fresh methyl laurate, having a viscosity of 2 cp, may be fed at a rate of 550 grams/second into a mixer where it is mixed with a 6400 grams/sec flow of recycled product and the resulting mixture is fed, at a temperature of about 38° C. (-100° F.) and a pressure of about 265 psia ( $1.8 \times 10^6$  pascal) into the top of 125 porous wall tubes arranged vertically in a bundle in a cylindrical reactor having an ID of about 20 inches. Each tube has an ID of about  $\frac{3}{8}$ " (1.91 cm), and has a 110 cm. length of porous metal comprising stainless steel fabricated by powder metallurgy and coated with zirconia to have a viscosity normalized permeance of about  $1.2 \times 10^{-3} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .

The tubes are each packed with inert glass balls, having a diameter of 0.320 cm., up to a distance of 10 cm. above the porous portion of each tube and also extending to the bottom of each tube, i.e., beyond the porous portion of the tube in the direction of reactant flow.

On the shell side of the reactor, liquid SO<sub>3</sub> may be introduced into the reactor, without mixing with recycled product, at a flow rate of about 205 grams/sec flow, and at a temperature of about 38° C. (-100° F.) and a pressure of about 350 psia ( $2.4 \times 10^6$  pascal) to pass through the porous tubes and react with the methyl laurate therein.

The resulting product stream leaving the reactor at a temperature of about 74° C. (-165° F.) and a pressure of about 65 psia ( $4.5 \times 10^5$  pascal) is fed through a heat exchanger similar to that described in Example I. The resulting sulfonated methyl laurate product will again be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

(b) Similarly, the reaction described in Example II (a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene, the corresponding linear alkylbenzenesulfonic acid is obtained.

- (c) Similarly, the reaction described in Example II(a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, and the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

### EXAMPLE III

#### Ester Sulfonation, Multiple Stages

- (a) To illustrate the use of multiple stages of the process of the invention, when products with particularly low levels of impurities are desired, three shell and tube reactors similar to those used in Examples I and II may be used. The porous wall portion of each tube would be 110 cm in length and the inner diameter of each would be 1.91 cm (¾). The porous portion of each tube may be fabricated from a stainless steel powder metallurgy and coated with zirconia to provide a viscosity normalized permeance of  $1.2 \times 10^{-9}$  cm<sup>3</sup> cp/cm<sup>2</sup> sec psi and each tube could be filled with 0.32 cm diameter inert glass balls to 10 cm above and below the porous portion of the tube. In each reactor, the tubes would be located in a 50.8 cm (20 in) diameter shell. Each reactor may be connected to a heat exchanger having tubes with a diameter of 1.91 cm ID filled with the same inert 0.32 cm diameter spherical glass mixing elements used in the reactors. The length of the tubes could be varied for different stages.

In the first stage, a 550 grams/sec flow of fresh methyl laurate may be mixed with 2900 grams/sec of cooled recycled product from the first stage and introduced into a 46 tube reactor first stage at a temperature of 38° C. (100° F) and a pressure of 155 psia ( $1.1 \times 10^6$  pascal).

About 50% (103 grams/sec) of the total SO<sub>3</sub> is introduced as a liquid into the shell side of the first stage reactor at 350 psia and a temperature of 38° C. The resultant product flow, having a temperature of about 74° C. (165° F) and a pressure of 65 psia ( $4.5 \times 10^5$  pascal), is fed into a heat exchange containing 45 of the 0.6 meter long tubes filled with mixing elements.

From the output of the first stage heat exchanger, 655 grams/sec is mixed with 1775 grams/sec of cooled product stream from the second stage and fed into 36 tubes comprising the second stage reactor at a temperature of 38° C. (100° F) and 200 psia ( $1.4 \times 10^6$  pascal). The other 2900 grams/sec of cooled product from the first stage may be recycled back to the first stage reactor as described above.

About 35% (72 grams/sec) of the total amount of SO<sub>3</sub> is introduced as a liquid into the shell side of the second stage reactor at 350 psia ( $2.4 \times 10^6$  pascal) which will result in a product flow exiting the second stage reactor at 65 psia ( $4.5 \times 10^5$  pascal) and a temperature of 74° C. (165° F). This product flow is then cooled by feeding it into 115 1.3 meter long mixing element-filled tubes in the second stage heat exchanger.

From the second stage recirculating loop downstream of the second stage heat exchanger, 725 grams/sec of product flow is mixed with 320 grams/sec of cooled product from the third stage and introduced into the 19 tube third stage reactor at a temperature of 38° C. (100° F) and a pressure of 265 psia ( $1.8 \times 10^6$  pascal). In this stage the remaining 15% of the SO<sub>3</sub> is introduced at a temperature of 38° C. and a pressure of 115 psia ( $1.1 \times 10^6$  pascal).

The product flow from the third stage reactor tubes leaves the reactor at 65 psia and 74° C. (165° F) and enters a heat exchanger containing 200 of the 2.3 meter tubes which are also filled with mixing elements. From the recirculating loop

coming from this third heat exchanger, 760 grams/sec of product are withdrawn, while the remaining 320 grams/sec of cooled product are recycled as previously described.

- The resulting sulfonated methyl laurate product will again be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

- (b) Similarly, the reaction described in Example III (a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene, the corresponding linear alkylbenzenesulfonic acid is obtained.

- (c) Similarly, the reaction described in Example III (a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, and the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

### EXAMPLE IV

#### Ester Sulfonation, Small Temperature Increase

- (a) To illustrate a modification of the process of the invention, where all of the SO<sub>3</sub> is introduced in one stage with a very low rise in temperature because of the high recycle rate, and a second stage is provided operating at a substantially higher temperature to allow any rearrangement of SO<sub>3</sub> among the molecules in the product from the first reactor stage, methyl laurate may be introduced into a reactor containing 200 tubes, each having the same dimensions and viscosity normalized permeance as in Example II.

The flow rate of fresh methyl laurate is also the same as in Example II, i.e. 550 grams/sec, but the amount of recycled product blended with the methyl laurate prior to introduction into the tubes is 10,750 grams/second, i.e., much higher than Example II, resulting in more thermal mass and, therefore, a commensurate reduction in the temperature rise from the fixed exothermic heat generated. The combined stream enters the tubes of the reactor at 38° C. (100° F) and 285 psia ( $1.96 \times 10^6$  pascal).

On the shell side of the reactor a stream of 205 grams of liquid SO<sub>3</sub> is introduced into the reactor at a temperature of 38° C. (100° F) and a pressure of 290 psia ( $2.0 \times 10^6$  pascal).

The product flow exiting the reactor then is circulated through the same mixing element-filled heat exchanger as in Example I and a product flow of about 760 grams/sec is withdrawn from output of the heat exchanger (with the balance recycled back to the reactor), mixed with a flow of about 6000 grams/sec of recycled product from a mixing tank, and pumped to the tube side of a heat exchanger where it is heated to have an exit temperature of 82° C. (180° F). This flow goes to the mixing tank which is sized to have a residence time of about 15 minutes. This time at elevated temperature allows any rearrangement of the materials in the product to closely approach equilibrium. The product is continuously withdrawn from the mixing tank at 760 grams/sec and cooled for storage or use.

In this regard, it should be noted that such a mixing tank is filled with the product from the last operation. The first time the apparatus is started, the tank is filled from the low temperature reactor. The mixing tank can have any type of stirring or agitation means within it, including mixing elements. For example, some molecules could contain two attached SO<sub>3</sub> groups and other molecules have no SO<sub>3</sub> groups attached. The breaking of a SO<sub>3</sub> group away from a molecule with two such groups and the combination of an

SO<sub>3</sub> group with a molecule without an SO<sub>3</sub> group on it would not generate substantial net heat in the mixing tank.

Again, the resulting product will be uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

(b) Similarly, the reaction described in Example IV (a) above is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of linear alkylbenzene the corresponding linear alkylbenzenesulfonic acid is obtained.

(c) Similarly, when the reaction described above in Example IV (a) is repeated except that the methyl laurate is replaced by a stoichiometrically equivalent amount of phenol, the corresponding mixture of hydroxybenzenesulfonic acids are obtained.

#### EXAMPLE V

##### Alcohol and Ethylene Oxide

(a) Fresh tridecyl alcohol, having a viscosity of 1 cp, may be fed at a rate of 270 grams/second into a mixer where it is mixed with a 12,300 grams/sec flow of recycled product and the resulting mixture is fed, at a temperature of about 121° C. (-250° F.) and a pressure of about 80 psia (5.5x10<sup>6</sup> pascal) into the top of 585 porous wall tubes arranged vertically in a bundle in a cylindrical reactor having an ID of about 30 inches. Each tube has an ID of about ¾" (1.59 cm), and has a 100 cm. length of porous metal comprising stainless steel fabricated by powder metallurgy and coated with zirconia to have a viscosity normalized permeance of about 1.2x10<sup>-8</sup> cm<sup>3</sup> cp/cm<sup>2</sup> sec psi.

The tubes are each packed with inert glass balls, having a diameter of 0.265 cm., up to a distance of 10 cm. above the porous portion of each tube and also extending to the bottom of each tube, i.e., beyond the porous portion of the tube in the direction of reactant flow.

On the shell side of the reactor, gaseous ethylene oxide may be introduced into the reactor, without mixing with recycled product, at a flow rate of about 532 grams/sec flow, and at a temperature of about 121° C. (-250° F.), and a pressure of about 250 psia (1.7x10<sup>7</sup> pascal) to pass through the porous tubes and react with the tridecyl alcohol therein.

The resulting product stream leaving the reactor at a temperature of about 199° C. (-300° F.) and a pressure of about 65 psia (4.5x10<sup>6</sup> pascal) is fed through a heat exchanger similar to that described in Example I. The resulting ethoxylated tridecyl alcohol product will have a very unitary product distribution and be low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

Thus, the present invention provides a process for carrying out an exothermic process wherein the flow of second reactant into the reaction zone is controlled, to thereby control the reaction and the amount of exothermic heat generated, by the use of a porous barrier which restricts the amount of second reactant flowing across the porous barrier into the reaction zone. Such control of the reaction and generation of exothermic heat, while providing adequate mixing of the reactants in the reaction zone to ensure homogeneous reaction and heat generation in the reaction zone, results in a product which, as mentioned above in the examples, is uniform and low in unwanted products and substantially higher in quality than that obtained from state of the art reactor technology.

While the present invention has been described with reference to the specific embodiments thereof, it should be

understood by those skilled in the art of chemical processing and control of an exothermic reaction in a reaction zone by use of a porous barrier between a first reactant and a second reactant having mixing elements in the reaction zone as described herein. The use of a porous barrier and mixing elements in chemical processing applications is such that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the present invention. In addition, many modifications may be made to adapt a particular situation, material, or composition of matter, process, process step or steps, or the present objective to the spirit and scope of this invention, without departing from its essential teachings.

We claim:

1. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

(a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;

(b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone which is separated from said first reactor zone by a porous wall which is capable of being penetrated by said second reactant at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reactor zone at corresponding locations along the length of said porous wall, to thereby inhibit any flow of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone; wherein said one or more second reactants pass once through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone,

wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about 10<sup>-6</sup> to about 5x10<sup>-2</sup> cm<sup>3</sup> cp/cm<sup>2</sup> sec psi.

2. The process of claim 1 wherein a portion of the product flow from said reactor is recycled back and blended with said one or more first reactants being fed into said first reactor zone.

3. The process of claim 1 wherein a portion of the product flow from said reactor is recycled back and blended with said one or more second reactants being fed into said second reactor zone.

4. The process of claim 1 wherein at least one of said reactants is a liquid.

5. The process of claim 4 wherein at least one of said one or more said first reactants is a liquid.

6. The process of claim 4 wherein at least one of said one or more second reactants is a liquid.

7. The process of claim 4 wherein at least one of said one or more first reactants is a liquid and at least one of said one or more second reactants is a liquid.

8. The process of claim 1 wherein the temperature of each of said reactants being fed into the respective reaction zones is within a range of from about  $-50^{\circ}\text{C}$ . to about  $500^{\circ}\text{C}$ .

9. The process of claim 1 wherein the pressure of each of said first reactants and said second reactants being fed into the respective reaction zones is within a range of from about 14 psia to about 1000 psia, with the pressure of said one or more second reactants being greater than the pressure of said one or more first reactants.

10. The process of claim 1 wherein all or a portion of said product is recycled back to said first reactor zone.

11. The process of claim 10 wherein all or a portion of said product is cooled and then recycled back to said first reactor zone.

12. The process of claim 1 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reactor zone.

13. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

(a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;

(b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone which is separated from said first reactor zone by a porous wall which is capable of being penetrated by said second reactant at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reactor zone at corresponding locations along the length of said porous wall, to thereby inhibit any flow of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone; wherein said one or more second reactants pass once through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone, wherein said product flow from said reactor is first passed through a heat exchanger before said portion of said product flow is recycled back and blended with said one or more first reactants being fed into said first reactor zone,

wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .

14. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

(a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;

(b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone which is separated from said first reactor zone by a porous wall which is capable of being penetrated by said second reactant at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reactor zone at corresponding locations along the length of said porous wall, to thereby inhibit any flow of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone; wherein said one or more second reactants pass once through said porous wall to contact said one or more first reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone,

wherein a portion of the product flow from said reactor is recycled back and blended with said one or more second reactants being fed into said second reactor zone, and

wherein said product flow from said reactor is first passed through a heat exchanger before said portion of said product flow is recycled back and blended with said one or more second reactants being fed into said second reactor zone,

wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .

15. A process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants, which process comprises:

(a) feeding into a first reactor zone having mixing elements therein one or more first reactants at a first pressure;

(b) feeding one or more second reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall which is capable of being penetrated by said one or more second reactants at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reactor zone at corresponding locations along said porous wall, to thereby inhibit any flow of the components of said first reactor zone which are selected from the group con-

sisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone;

wherein said one or more second reactants pass through said porous wall to contact said one or more first liquid reactants in said first reactor zone and form said reaction product fluid comprising a liquid, a gas or combinations thereof in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone, and the temperature of the reaction is between about 0° and 400° C.,

wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2}$  cm<sup>2</sup> cp/cm<sup>2</sup> sec psi.

16. The process of claim 1 wherein said mixing elements in said first reactor zone have at least one dimension which is equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone wherein said one dimension and said largest dimension are measured in the dimension which is perpendicular to the flow of said one or more first reactants through said first reactor zone.

17. The process of claim 16 wherein said mixing elements in said first reactor zone have at least one dimension equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone normal to the flow of said one or more first reactants through said first reactor zone.

18. The process of claim 15 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reactor zone.

19. The process of claim 1 wherein the reaction occurring in zone one is selected from the group consisting of oxidation, sulfonation, hydrogenation, halogenation, ethoxylation, sulfation, nitration, and polymerization.

20. The process of claim 1 wherein the reaction is oxidation.

21. The process of claim 1 wherein the reaction is sulfonation.

22. The process of claim 1 wherein the reaction is hydrogenation.

23. The process of claim 1 wherein the reaction is halogenation.

24. The process of claim 1 wherein the reaction is nitration.

25. The process of claim 1 wherein the reaction is polymerization.

26. An exothermic process for forming a reaction product fluid by reaction of one or more first liquid reactants with one or more second liquid reactants, which process comprises:

(a) feeding one or more first liquid reactants at a first pressure through a first reactor zone having mixing elements therein;

(b) feeding one or more second liquid reactants at a second pressure higher than said first pressure into a second reactor zone which is separated from said first reactor zone by a porous wall which is capable of being penetrated at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reactor zone higher than the pressure in said first reaction zone

at corresponding locations of said porous wall, to thereby inhibit any flow of the components of said first reactor zone one which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone;

wherein said one or more second liquid reactants pass once through said porous wall to contact said one or more first liquid reactants in said first reactor zone and form said reaction product fluid only in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone,

wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2}$  cm<sup>2</sup> cp/cm<sup>2</sup> sec psi.

27. The process of claim 26 wherein said mixing elements in said first reactor zone have at least one dimension which is equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone wherein said one dimension and said largest dimension are measured in the dimension which is perpendicular to the flow of said one or more first reactants through said first reactor zone.

28. An exothermic process for forming a reaction product fluid by reaction of one or more liquid first reactants with one or more second reactants, at least one of which is gaseous, which comprises:

(a) feeding said one or more liquid first reactants at a first pressure through a first reactor zone having mixing elements therein;

(b) feeding said one or more second reactant, at least one of which is gaseous at ambient conditions, at a second pressure higher than said first pressure into a second reactor zone which is separated from said first reactor zone by a porous wall which is capable of being penetrated by said one or more second reactants at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reaction zone at corresponding locations of said porous wall, to thereby inhibit any flow back of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone;

wherein said one or more second reactants pass once through said porous wall to contact said one or more liquid first reactants in said first reactor zone and form said reaction product fluid only in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone,

wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2}$  cm<sup>2</sup> cp/cm<sup>2</sup> sec psi.

29. The process of claim 28 wherein said mixing elements in said first reactor zone have at least one dimension equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone normal to the flow of said one or more liquid first reactants through said first reactor zone.

30. The process of claim 29 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reactor zone.

31. An exothermic process for forming a reaction product fluid by reaction of one or more first reactants and one or more second reactants which comprises:

(a) feeding a first reactant at a first pressure through a first reactor zone containing mixing elements having at least one dimension which is equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone wherein said one dimension and said largest dimension are measured in the dimension which is perpendicular to the flow of said first reactant through said first reactor zone;

(b) feeding a second reactant at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall having multiple openings capable of being penetrated by said second reactant at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reaction zone at corresponding locations of said porous wall, to thereby inhibit any flow of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reactor zone to said second reactor zone;

whereby said second reactant passes through said porous wall to contact said first reactant in said first reactor zone and form said reaction product only in said first reactor zone, and the components of said first reactor zone one which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone, wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .

32. The process of claim 31 wherein at least one of said reactants is a liquid.

33. A process for forming a reaction product fluid by reaction of a first liquid reactant with a second liquid reactant, which process comprises:

(a) feeding a first liquid reactant at a first pressure into a first reactor zone containing particles having at least one dimension which is equal to from about  $\frac{1}{2}$  to about  $\frac{1}{100}$  of the largest dimension of said first reactor zone wherein said one dimension and said largest dimension are measured perpendicular to the flow of said liquid reactant through said first reactor zone;

(b) feeding a second liquid reactant at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall capable of being penetrated by said second liquid

reactant at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone higher than the pressure in said first reaction zone at corresponding locations of said porous wall, to thereby inhibit any flow through said porous wall from said first reactor zone to said second reactor zone, of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof;

whereby said second liquid reactant passes through said porous wall to contact said first liquid reactant in said first reactor zone and form said reaction product fluid comprising a liquid, a gas, or combinations thereof only in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone, wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .

34. The process of claim 33 wherein said porous wall through which said second liquid reactant passes into said first reactor zone has a viscosity normalized permeability ranging from about  $5 \times 10^{-6}$  to about  $5 \times 10^{-2} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec}$ .

35. The process of claim 34 wherein said porous wall comprises one or more porous tubes which separate said first reactor zone from said second reactor zone.

36. A process for forming a product by reaction of one or more first reactants and one or more second reactants which comprises:

(a) feeding into a first reactor zone having mixing elements therein said one or more first reactants at a first pressure;

(b) feeding one or more of said second reactants at a second pressure higher than said first pressure into a second reactor zone separated from said first reactor zone by a porous wall which is capable of being penetrated by said second reactant at multiple sites to produce in said first reactor zone a resulting mixture having components selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted said second reactant and combinations thereof; and

(c) maintaining the pressure within said second reaction zone at all locations of said porous wall higher than the pressure in said first reaction zone at corresponding locations of said porous wall, to thereby inhibit any flow of the components of said first reactor zone which are selected from the group consisting of said reaction product fluid, unreacted said first reactant, unreacted second reactant and combinations thereof through said porous wall from said first reaction zone to said second reaction zone;

wherein said one or more second reactants will pass through said porous wall to contact said one or more first reactants in said first reactor zone and form said product only in said first reactor zone, and the components of said first reactor zone which are selected from the group consisting of said reaction product fluid,



- unreacted said first reactant, unreacted said second reactant and combinations thereof exit only from said first reactor zone wherein the flow of the first reactant is pulsed flowed at a rate which changes the flow rate from about a maximum flow rate in one direction to zero flow and then to about 20% of the maximum rate in the reverse direction and thereafter returns to the maximum flow rate in the original direction, wherein said porous wall through which said one or more second reactants passes into said first reactor zone has a viscosity normalized permeability ranging from about  $10^{-6}$  to about  $5 \times 10^{-2} \text{ cm}^3 \text{ cp/cm}^2 \text{ sec psi}$ .
37. The process of claim 36 wherein the flow changes in a pulsed manner from about the maximum flow down to about 50% of the maximum flow rate and returns to about the maximum flow rate in the original direction.
38. The process of claim 36 wherein in step (c) the rate of flow of the first reactant is pulsed to about 80% of the maximum flow rate and then returns to about the maximum flow rate in the original direction.
39. The process of claim 36 wherein in step (c) the rate of the flow of the first reactant is pulsed down to about 20% of the maximum rate of flow and then returns to about the maximum flow rate in the original direction.
40. The process of claim 36 wherein the pulsed flow has a flow cycle time of between about 0.1 and 1000 seconds.
41. The process of claim 1 wherein the process comprises step (d), (e) and (f);
- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) thereby creating a reaction product liquid; and
- (f) recycling all, a portion or none of the reaction product liquid of step (e), which is now depleted of volatile reactants, reaction products or a combination thereof, to the first reactor zone of step (a).
42. The process of claim 15 wherein the process comprises step (d), (e) and (f);
- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) thereby creating a reaction product liquid; and
- (f) recycling all, a portion or none of the reaction product liquid of step (e), which is now depleted of volatile reactants, reaction products or a combination thereof, to the first reactor zone of step (a).
43. The process of claim 26 wherein the process comprises step (d), (e) and (f);

- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) thereby creating a reaction product liquid; and
- (f) recycling all, a portion or none of the reaction product liquid of step (e), which is now depleted of volatile reactants, reaction products or a combination thereof, to the first reactor zone of step (a).
44. The process of claim 28 wherein the process comprises step (d), (e) and (f);
- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) thereby creating a reaction product liquid; and
- (f) recycling all, a portion, or none of the reaction product liquid of step (e) which is now depleted of volatile reactants, reaction products or a combination thereof, to the first reactor zone of step (a).
45. The process of claim 31 wherein the process comprises step (d), (e) and (f);
- (d) conveying a portion of the reaction product of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) thereby creating a reaction product liquid; and
- (f) recycling all, a portion or none of the reaction product liquid of step (e) which is now depleted of volatile reactants, reaction products or a combination thereof, to the first reactor zone of step (a).
46. The process of claim 33 wherein the process comprises step (d), (e) and (f);
- (d) conveying a portion of the reaction product fluid of step (c) to an evaporator;
- (e) separating volatile reactants or volatile reaction products wherein the vapor pressure of the volatile reactants or volatile reaction products is about 1 mm of Hg or higher at the temperature of the reaction in step (c) thereby creating a reaction product liquid; and
- (f) recycling all, a portion or none of the reaction product liquid of step (e), now depleted of volatile reactants, reaction products or a combination thereof, to the first reactor zone of step (a).

\* \* \* \* \*



US005445801A

**United States Patent** [19][11] **Patent Number:** **5,445,801****Pisoni**[45] **Date of Patent:** **Aug. 29, 1995**[54] **MULTITUBE FALLING-FILM REACTOR**4,059,621 11/1977 Johnson, Jr. .... 562/123  
4,183,897 1/1980 Lanteri ..... 261/112.1[75] **Inventor:** Carlo Pisoni, Busto Arsizio, Italy**FOREIGN PATENT DOCUMENTS**[73] **Assignee:** Meccaniche Moderne S.r.l. Chemical  
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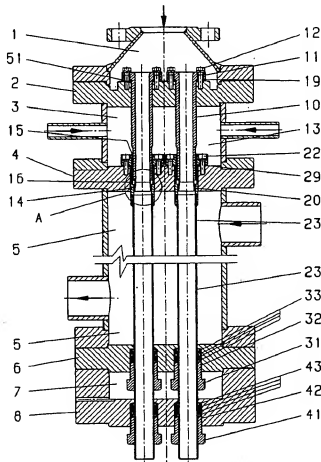
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[21] **Appl. No.:** 63,250*Primary Examiner*—Robert J. Warden[22] **Filed:** May 18, 1993*Assistant Examiner*—L. M. Crawford*Attorney, Agent, or Firm*—Bucknam and Archer[30] **Foreign Application Priority Data**[57] **ABSTRACT**

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[51] **Int. Cl.** ..... B01J 10/02[52] **U.S. Cl.** ..... 422/129; 261/112.1;  
422/129; 562/123[58] **Field of Search** ..... 422/129, 198, 200, 201,  
422/188, 196-197; 261/108, 112.1, 153, 160;  
562/123[56] **References Cited****U.S. PATENT DOCUMENTS**3,531,518 9/1970 Ohren et al. .... 562/123  
3,535,339 10/1970 Beyer et al. .... 562/123  
3,667,919 6/1972 Denzler et al. .... 422/310  
3,918,917 11/1975 Ashina et al. .... 261/112.1  
4,036,596 7/1977 Ogoshi et al. .... 261/112.1

Multitube falling-film reactor for the continuous sulfonation and sulfation of fluid-state organic substances by reaction with gaseous sulphuric anhydride (SO<sub>3</sub>), has each tubular element non-permanently fixed to the plates and has a nozzle (10) fitted in a sleeve (20) integral with a reaction tube (23). The nozzle (10) can slide within the sleeve (20) and may be placed at different heights with respect to the latter, forming with the end-piece (14) a cylindrical crown opening (18) of fixed width and variable height. Such arrangement permits to control the delivery of the fluid to be sulfonated. The opposite end of each tube (23) fits into a double-plate seal system.

**5 Claims, 3 Drawing Sheets**





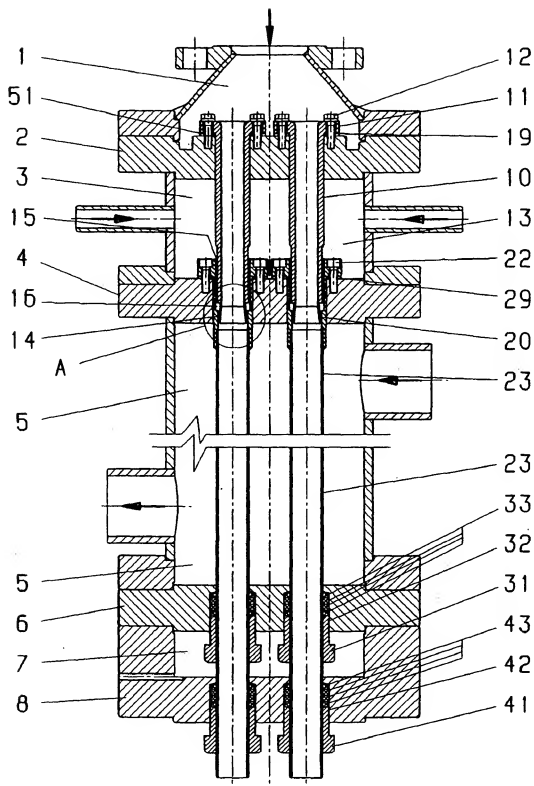


Fig. 4

## MULTITUBE FALLING-FILM REACTOR

## FIELD OF THE INVENTION

This invention refers to a multitube falling-film reactor, utilizable in particular for the continuous sulfonation and the sulfation of fluid-state organic substances by reaction with gaseous sulphuric anhydride ( $\text{SO}_3$ ).

Reactors of this type are well known in the art and are available on the market. They are essentially constituted by a nest of tubes wherein the tubes are permanently fixed to at least one plate.

The organic substance and the  $\text{SO}_3$ , opportunely diluted with air at a concentration of about 4%, are fed from above within the tubes, while a cooling fluid, generally water, is provided externally to the tubes to absorb the heat of the reaction (exothermic). In order to obtain high yields and a sulfonated or sulfated product of good quality, reaction must take place uniformly in each tube of the reactor.

To obtain this result, the reagents should be distributed homogeneously and constantly in each tube of the reactor. However, while for  $\text{SO}_3$  this uniform distribution takes place spontaneously, as this reagent is fed at a constant pressure in the gaseous phase, for the organic substance, on the contrary, a control system must be provided in the various tubes in order to obtain the necessary distribution uniformity. At present, various control systems are utilized, all of which have a distributor on top of each tube provided with a slit or orifice whose section can be mechanically adjustable in various ways.

These systems permit a poorly precise control of the delivery. Actually, minor variations in the passage sections suffice to produce rather high delivery variations, which prevent the organic substance from reaching an optimum distribution uniformity in all the tubes. Besides, the known reactors show another drawback which adds to the above mentioned inconvenience. In fact, they are produced with tubes that are permanently fixed to the plates and therefore they cannot be easily removed, should they break. As a consequence, maintenance operations are needed which are rather wearisome and lengthy, to have the reactor repaired.

Now, the applicant has devised the multitube falling-film reactor subject of this invention, utilizable in particular for sulfonation and sulfation reactions, which permits to eliminate all the above mentioned drawbacks of the known reactors of the known types.

## SUMMARY OF THE INVENTION

An object of this invention is therefore a reactor comprising:

a) a very simple and precise control system of the delivery of the fluid-state organic composition to be sulfonated or sulfated, based on the formation, on top of each tube, of a cylindrical crown opening placed between a concentric nozzle and sleeve unit. The internal nozzle can slide within the external sleeve, integral with a reaction tube and may be placed at various heights. Such arrangement permits to have fixed width and variable height openings, which allow for variations in the charge loss in the splits, such as to produce flow variations, utilizable to control and make uniform the fluid flow in the various tubes of the reactor. The precision and accuracy of this control system ensue from the fact that even minor delivery variations—allowing for very exact and easily reproducible calibrations—can be

obtained through rather high and easily controllable vertical shifts of the nozzle;

b) nest of tubes non permanently fixed to the plates, but blocked to the latter by means of systems with flanges, ring nuts and seals. Such tubes can be easily taken out and may be replaced in a very short time;

c) adoption on the reactor outlet side (lower side) of a double plate seal system, which permits to avoid, in case of loss from the first plate, any infiltration of cooling water into the reaction fluid, which would cause its pollution and the onset of corrosion phenomena downstream of the reactor.

## BRIEF DESCRIPTION OF THE DRAWINGS

The structures of such a reactor object of this invention shall clearly appear from the following detailed description, wherein reference is made to the attached drawings which represent a preferred embodiment, to be construed as a non-limitative example, and wherein:

FIG. 1 is a longitudinal section of a tubular element of the multitube reactor object of this invention;

FIG. 2 is an enlargement of the II—II cross section of FIG. 1; and

FIG. 3 is an enlargement of detail A of FIG. 1.

FIG. 4 is a longitudinal section of the reactor of this invention.

With reference to the above drawings, the reactor is represented, by way of example, by a single tubular element.

A top cap, bounds a chamber 1 of distribution of the gaseous  $\text{SO}_3$  in the various tubes, placed upon a first top plate 2. Nozzles 10 fit in special holes of said plate, said nozzles having each an edge 11, utilized to fix the nozzle to said plate by means of screws 12 and gaskets 13. Each nozzle 10 comprises a lower part 13 having a toothed-wheel-shaped radial section and a lower end-piece 14.

Such lower part 13 fits into a sleeve 20, which, in its turn, fits into a special hole provided in a second top plate 4, to which it is fixed along edge 21 by means of screws 22 and gaskets 29. At both ends of said sleeve 20, projecting under plate 4, a reaction tube 23 is connected. This connection is made in such a way as to cause the internal wall of said tube 23 to be flush with the internal wall of said sleeve 20.

A chamber 3 of distribution of the fluid to be sulfonated or sulfated is placed between the first top plate 2 and the second top plate 4. From this chamber, the fluid flows in the longitudinal channels 15 provided in the lower part 13 of nozzle 10, collects in a cavity 16 and then flows down from a cylindrical crown-shaped opening 18 provided between the inner wall of the lower part of sleeve 20 and the external wall of end-piece 14 of nozzle 10, forming a film that flows down along the internal wall of tube 23 and that reacts with  $\text{SO}_3$  which moves in concurrent.

The width of each circular crown of each opening 18 is fixed and calibrated in function of the fluid to be fed.

Generally, it has a constant value in all tubes, comprised between 0.15 and 0.50 mm, and preferably between 0.25 and 0.35 mm. On the contrary, the height of each opening 18 can be changed by raising or lowering nozzle 10, so as to obtain charge losses through said opening, and, therefore, variations in the delivery of fluid fed to reaction tube 23. Such an arrangement permits to calibrate, with the utmost precision and accuracy, the fluid delivery into the various tubes of the reactor, making the distribution uniform in each tube

and making up in this way for the flow differences which would create in the tubes, due to unavoidable, however minor, width differences in the various openings 18. In practice, such calibration operation is made by utilizing varying thickness strips 51, calibrated to thickness differences of 0.01-2.0 mm, which are fitted between the edge of each nozzle 10 and gasket 19, until a uniform fluid flow is obtained in all tubes.

The lower end of each tube 23 is fitted in a double plate system. In fact, the reactor comprises a first lower plate 6 and a second lower plate 8, both of them having non permanently fixed through-tubes. On each tube 23, the seal is provided respectively by braid-gaskets 33 and 43, which are set against tube 23 by ring nuts 31 and 41, when these latter are screwed, through threads 32 and 42 to said plates. Such double plate system prevents any possible infiltration of the pressurized cooling water in zone 5—provided on the outside of the tubes—from ending up in the reaction substance, giving rise in this way to the aforementioned problems.

This infiltration would cause the cooling water to collect on the fact in the air gap at atmospheric pressure in zone 7 on the reactor outside, between the two plates 6 and 8.

The reactor according to the above described invention permits an easy and rapid taking out of any tube, if a change should be needed.

While the invention has been described with reference to a specific embodiment, many alternatives and changes may be obviously made by the experts in the light of the above description. Hence the invention embraces all the alternatives and changes which fall within the spirit and protection scope of the following claims.

#### I claim:

1. A multitube falling-film reactor for the continuous sulfonation and sulfation of a liquid organic substance by reaction with gaseous sulphuric anhydride  $\text{SO}_3$ , consisting essentially of a plurality of tubular elements means for feeding said liquid organic substance, each tubular element consisting essentially of a nozzle (10) fitted in a first top plate (2); said nozzle comprising, a lower part (13), a sleeve (20) fitted in a second top plate (4), said lower part of said nozzle fitting into said sleeve; a reaction tube (23) fixed to said sleeve (20) and projecting under said second top plate (4); said sleeve having an internal surface and a lower part, said reaction tube having a lower end and an internal surface and being placed in such a way as to cause its internal surface to be flush with said internal surface of said sleeve (20), said lower end of said reaction tube fitting into a double plate system comprising plates (6) and (8), said means for feeding said liquid organic substance is provided

with a first distribution chamber (3) placed between said first and second top plates (2) and (4) for feeding said liquid organic substance, said lower part of said nozzle is provided with longitudinal channels (15), defined by said lower part of said nozzle and said internal surface of said sleeve, said liquid organic substance flows through said longitudinal channels (15), collects in a cavity (16), said nozzle (10) has a lower end piece (14), said lower end piece having an external wall, a cylindrical crown-shaped opening (18) being provided between said inner wall of said lower part of said sleeve (20) and said external wall of said lower end piece (14), said opening (18) having constant width and a lower end, said liquid organic substance then flowing down from said cylindrical-crown-shaped opening (18), forming a fluid film which flows down along said internal walls of said reaction tube (23), where it reacts with said gaseous  $\text{SO}_3$  which moves concurrently upon said first top plate (2) and under a top cap for introducing  $\text{SO}_3$  at the level of said lower end of said opening (18), wherein said longitudinal channels (15) are defined by a toothed profile radial section of the lower part of said nozzle and said nozzle is adapted to slide within said sleeve (20) and may be placed at different heights.

2. The reactor according to claim 1 which is provided with steel strips (51) calibrated with thickness differences of 0.01-2 mm; said nozzle (10) has an edge, said steel strips are fitted between said edge and a gasket and wherein the height of said opening (18) is varied by raising or lowering said nozzle (10) by means of said steel strips (51), whereby variations in the flow of said liquid organic substance are obtained and the flow of said liquid organic substance becomes uniform in said plurality of tubular elements.

3. The reactor according to claim 2, wherein said nozzle has an edge (11), a gasket (19) and a screw (12) fixing said nozzle to said first top plate (2), said reactor is provided with steel strips (51) and calibrated with thickness differences of 0.01-2.0 mm, said strips being fitted between said edge (11) and said gasket (19), whereby variations in the flow of said liquid organic substance are obtained and the flow to all the tubes of said reactor is uniform.

4. The reactor according to claim 3, wherein said opening (18) has a width between 0.25 and 0.35 mm in all said tubular elements.

5. The reactor according to claim 4, wherein said nozzle (10) and said sleeve (20) are not permanently fixed to said first and second top plates (2) and (4) respectively.

\* \* \* \* \*

March 26, 1968

A. J. DE ROSSET

3,375,288

DEHYDROGENATION OF HYDROCARBONS AT HIGH CONVERSION LEVELS

Filed Oct. 28, 1964

Figure 1

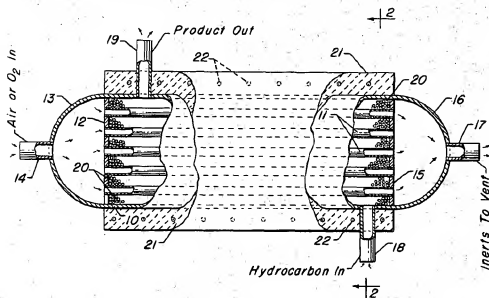
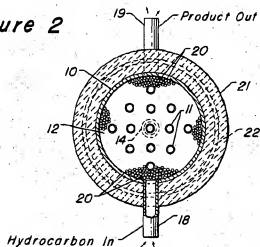


Figure 2



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3,375,288  
**DEHYDROGENATION OF HYDROCARBONS  
AT HIGH CONVERSION LEVELS**  
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corporation of Delaware  
Filed Oct. 28, 1964, Ser. No. 407,450  
9 Claims. (Cl. 260-659)

## ABSTRACT OF THE DISCLOSURE

A hydrocarbon is subjected to dehydrogenation in contact with one side of a silver membrane. An oxygen-containing gas is maintained in contact with the other side of the membrane. Oxygen is diffused through the membrane to oxidize the resulting free hydrogen, liberated during the course of the dehydrogenation, thereby lowering the hydrogen partial pressure of the reaction mixture. This permits the reaction to proceed at a relatively low temperature and with high selectivity toward the desired less saturated hydrocarbon product.

This invention relates to an improved process for the dehydrogenation of hydrocarbons. More particularly, the invention is directed to a method for reducing the hydrogen activity of the dehydrogenation equilibrium mixture whereby to increase the equilibrium ratio of the product. This technique permits the use of substantially lower dehydrogenation temperatures than are conventionally employed and achieves greater yields per pass and higher selectivity.

The reduction of hydrogen activity is accomplished through the use of a thin metallic silver wall or membrane one side of which contacts the dehydrogenation zone proper and the other side of which contacts a free oxygen-containing atmosphere. The membrane is arranged to isolate the dehydrogenation zone from the oxygen-containing atmosphere while at the same time affording a diffusive flow path therebetween. The silver membrane has a high permeability to oxygen, whereby the oxygen diffuses through the membrane to oxidize the free hydrogen liberated in the dehydrogenation zone. Because the oxygen transfer is diffusion controlled, the combustion of hydrogen takes place in a thin bimolecular oxidation zone along the surface of the membrane and does not propagate itself generally throughout the dehydrogenation zone. The selective removal of hydrogen decreases its partial pressure and the dehydrogenation reaction proceeds to completion at a relatively low temperature.

The process of this invention may be advantageously practiced by means of a novel tubular reactor comprising inner and outer tubes, at least a portion of the wall of the inner tube consisting of a thin silver membrane adapted to permit diffusive flow of oxygen therethrough, together with means for heating the tubes to dehydrogenation temperatures, means for introducing a gaseous hydrocarbon feed into one of said tubes and for withdrawing product therefrom, and means for introducing an oxygen-containing gas into the other of said tubes. The interior of the inner tube may be the dehydrogenation zone and the annular space between the tubes may be the oxygen supply zone; conversely, the interior of the inner tube may be the oxygen supply zone and the annular space between the tubes may serve as the dehydrogenation zone. In a preferred embodiment of the apparatus, the reactor comprises a bundle of thin-walled silver tubes mounted within a single outer tube or shell, as in the furnace shell-and-tube heat exchanger. The increased surface area of the multiple tube design affords higher oxygen transfer rates. The dehydrogenation reaction may be carried out ther-

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mally or catalytically, preferably the latter. For thermal conversions, the dehydrogenation zone may be left empty or it may be filled with inert heat conductive packing or heat transfer pebbles. For catalytic conversions, the catalyst may be suitably deposited as a thin film upon the wall of the dehydrogenation zone, using vapor deposition or impregnation techniques; alternatively, the dehydrogenation zone may comprise a bed of catalyst particles. The various dehydrogenation catalysts suitable for use in the present invention are well known in the art and they include, for example, alumina, chromia-alumina, chromia-magnesia, chromia-beryllia-alumina, ferric-alumina, ferric-magnesia, platinum group metals in general, particularly platinum-alumina and nickel oxide-alumina, 15 oxides of strontium, barium and molybdenum, ortho-phosphoric acid, various alkali or alkaline earth metals, cupric oxide in combination with a stabilizer such as an oxide of silver, zinc, cadmium, cobalt or nickel. Typical compositions include, for example, 3-60% chromia on alumina, 10-20%  $\text{Fe}_2\text{O}_3$  on alumina, 30 chromia-10 20 beryllia-50 alumina, with any of the foregoing being promoted by the addition of 1-8% potassa or cupric oxide. Another composition suited for use in dehydrogenation reactions is 10-30%  $\text{Fe}_2\text{O}_3$  plus 3-8%  $\text{K}_2\text{O}$  plus 62-87% 25  $\text{CuO}$ . The particular composition of a given catalyst as it may be employed in the present invention will, of course, be determined in accordance with the particular feed stock, reaction conditions and extent of conversion desired, in a manner known to those skilled in the art.

The apparatus and process of this invention are generally applicable in the dehydrogenation of alkanes, alkenes and alkyl aromatics, and more particularly in the dehydrogenation of n-alkanes or iso-alkanes containing 3 3 to 6 carbon atoms per molecule to the corresponding n-alkenes or iso-alkenes or, in a single stage, to the corresponding n-alkadienes or iso-alkadienes; further, in the dehydrogenation of n-alkenes or iso-alkenes containing 3 5 to 6 carbon atoms per molecule to the corresponding n-alkadiene or iso-alkadiene, particularly the conjugated dienes; still further, in the dehydrogenation of an alkylbenzene or alkyl-naphthalene, in which the alkyl group contains 2 to 6 carbon atoms, to the alkylene benzene or alkylene naphthalene. Some of the more commercially 40 important conversions include, for example, the dehydrogenation of propane to propylene, n-butane to 1-butene, n-butane to 1,3-butadiene, 1-butene to 1,3-butadiene, cis-2-butene or trans-2-butene to 1,3-butadiene, 1-pentene to 1,3-pentadiene, 2-methyl-1-butene to 1,3-pentadiene, 2-ethyl-1-butene to 1,3-pentadiene, isopropylbenzene to methyl styrene, and ethyl-naphthalene to vinyl naphthalene.

Catalytic dehydrogenation processes of the prior art require relatively high temperatures to achieve commercially significant conversions, generally in the range of 1000°-1200° F. The present invention, on the other 45 hand, affords substantial conversions at lower temperatures, generally in the range of 800°-1000° F, when a catalyst is employed. Feed partial pressures may range from a new millimillimeter Hg absolute to 50 p.s.i.a. or more, and space velocities from 0.2 to 1000 volumes of hydrocarbon feed/volume of catalyst/hour.

It is, therefore, a further aspect of the invention to provide an improved process for the dehydrogenation of a hydrocarbon feed stock wherein the feed is reacted in a dehydrogenation zone under dehydrogenation conditions 50 to yield a less saturated hydrocarbon and free hydrogen, which improvement is specifically directed to reducing the hydrogen activity of the reaction mixture and which comprises contacting the reaction mixture, while undergoing dehydrogenation, with one side of a thin silver membrane, maintaining an oxygen-containing gas in contact with the other side of said membrane, and diffusing oxygen through

the membrane into the dehydrogenation zone to oxidize such free hydrogen and thereby lower its partial pressure so that the dehydrogenation of the hydrocarbon proceeds to completion at a relatively low temperature. This in turn affords a significantly increased level of conversion and higher selectivity toward the desired olefinic product.

The present invention may be more clearly understood by reference to the accompanying drawing, which illustrates a preferred apparatus for carrying out the process but it is not intended that the apparatus therein illustrated shall limit the scope of the invention to any greater extent than is required by the claims.

FIGURE 1 is a sectional view of a multiple tube reactor, FIGURE 2 is a transverse view of the apparatus of FIGURE 1, taken along line 2-2 of FIGURE 1.

With reference to FIGURES 1 and 2, the reactor is comprised of an outer shell 10 and an inner bundle of tubes 11. Tubes 11 typically have an outside diameter of 0.01 inch to 0.5 inch and a wall thickness of 0.001 inch to 0.01 inch, although greater or lesser diameters and thicknesses may be utilized when desired. The ends of tubes 11 are suitably rolled or welded to tube sheets 12 and 15. Tube sheet 12 and head 13 define an inlet manifold to which air or oxygen is introduced through an inlet conduit 14; tube sheet 15 together with head 16 define an outlet manifold from which inerts may be vented through conduit 17. A particle-form bed of dehydrogenation catalyst 20 is disposed outside tubes 11; alternatively, areas of the exterior surface of tubes 11 may be coated with dehydrogenation catalyst. Shell 10 is encased by a refractory block 21 which in turn may be heated by conventional means such as electric coils 22 embedded therein. Heat transfer from block 21 to the shell and tube assembly serves to maintain the reaction zone at the desired elevated temperature.

Hydrocarbon vapor feed is introduced into shell 10 through feed inlet conduit 18; the feed may be diluted with steam, nitrogen, carbon dioxide or other inert gas for partial pressure control in the usual manner. Dehydrogenation reaction product is withdrawn from the other end of shell 10 through an outlet conduit 19. A free oxygen-containing gas is introduced into inlet conduit 14; such oxygen-containing gas may be pure oxygen, air or a blend of oxygen with steam or nitrogen. The total pressure of the oxygen-containing gas within tubes 11 is maintained substantially above the total pressure existing outside tubes 11; for example, the pressure differential may range from about 10 p.s.i. to about 1000 p.s.i. depending upon the wall thickness of tubes 11. Obviously the pressure differential should not be so great as to cause rupture of the tubes. The pressure of the oxygen-containing gas may be conveniently controlled by means of a differential pressure controller sensing the pressure of the oxygen-containing gas and the pressure of the dehydrogenation zone and the difference therebetween utilized to regulate the flow of oxygen-containing gas. The flow of oxygen through the tube walls is essentially diffusion-controlled. If pure oxygen is employed, the outlet conduit 17 may be omitted whereby tubes 11 merely define a dead-ended volume of oxygen. However, where the oxygen-containing gas comprises inerts such as nitrogen, water vapor or carbon dioxide, it is preferred to maintain a continuous flow thereof through tubes 11 to prevent accumulation of inerts within the system and at the same time to facilitate pressure control of the oxygen-containing gas. Gas which is depleted in oxygen may be withdrawn from outlet conduit 17, enriched by addition of make-up oxygen, and recycled to inlet conduit 14. It is, of course, within the scope of the present invention to reverse the functions of the shell and tubes whereby the tubes serve as the dehydrogenation zone and air or other oxygen-containing gas is charged to the shell side of the reactor; with this latter construction, the interior surfaces of tubes 11 may be coated with a suitable dehydrogenation catalyst or the

tubes may be filled with a solid dehydrogenation catalyst distended upon a porous support or carrier.

The benefits afforded by the invention are further illustrated by the following specific examples. It is not intended, however, that the invention be limited to the particular reactants, catalysts or conditions specified therein.

#### EXAMPLE I

##### Butane dehydrogenation

A first tubular reactor, designated reactor A, is constructed as shown in the drawing. The outer shell has an inside diameter of 2.5 inches. The inner tube bundle is 2.25 inches in diameter and 24 inches long and comprises 500 silver tubes,  $\frac{1}{8}$  inch O.D. of 0.002 inch wall thickness. The tubes are welded to tube sheets which are sealed to the outer shell. A second tubular reactor, designated reactor B, is similarly constructed except that the inner tubes are conventionally formed of a fluid-impervious stainless steel. Each reactor is loaded with 1000 cc. of 20-40 mesh dehydrogenation catalyst having the composition  $5 \text{ Cr}_2\text{O}_3\text{-}95 \text{ Al}_2\text{O}_3$ . The reactors are installed in a thermostatically controlled muffle furnace. Gaseous butane is fed to the shell of each and air is passed through the tube bundle. The butane feed and air streams are pre-heated to reaction temperature before entering the reactor. The pressure of the air stream in the bundle is maintained at 700 p.s.i.a. Conditions and results for a 30 minute period of lined out operation are given in Table I below. All flows are gas volume corrected to standard conditions of temperature and pressure.

TABLE I

	Reactor	
	A	B
Silver Membrane.....	Yes	No
Temperature, ° F.....	875	850
Inlet butane pressure, p.s.i.a.....	14.4	14.5
Feed rate, cc./min.....	2,000	2,000
Air rate, cc./min.....	3,000	2,000
Butane conversion, mol percent.....	21.3	6.5
Selectivity to total 1-butene, percent.....	92	85

#### EXAMPLE II

##### Butene dehydrogenation

The two reactors of Example I are utilized with the following changes: each reactor is loaded with 1000 cc. of a dehydrogenation catalyst having the composition  $84 \text{ Fe}_2\text{O}_3\text{-}4 \text{ Cr}_2\text{O}_3\text{-}12 \text{ K}_2\text{CO}_3$ ; the feed is 97% 1-butene; means are provided for diluting the feed with 1000° F. steam. Conditions and results for a 30 minute period of lined out operation are given in Table II below.

TABLE II

	Reactor	
	A	B
Silver Membrane.....	Yes	No
Temperature, ° F.....	1,000	1,000
Inlet butene pressure, p.s.i.a.....	17.1	17.1
Feed rate, cc./min.....	1,800	1,500
Steam rate, cc./min.....	18,000	18,000
Air rate, cc./min.....	2,350	2,300
Butene conversion, mol percent.....	78.6	3.0
Selectivity to 1,3-butadiene, percent.....	94	

#### EXAMPLE III

##### Ethylbenzene dehydrogenation

The two reactors of Example I are utilized with the following changes: each reactor is loaded with 1000 cc. 20-40 mesh granular catalyst having the composition  $90 \text{ Fe}_2\text{O}_3\text{-}4 \text{ Cr}_2\text{O}_3\text{-}6 \text{ K}_2\text{CO}_3$ ; the feed is 98% ethylbenzene; means are provided for diluting the feed with 950° F. steam. Conditions and results for a 30 minute period of lined out operation are given in Table III below.

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TABLE III

	Reactor	
	A	B
Silver Membrane.....	Yes	No
Temperature, °F.....	950	950
Inlet ethylbenzene pressure, p.s.i.a.....	19.2	19.2
Feed rate, cc./min.....	2	2
Steam rate, cc./min.....	22.6	22.6
Air rate, cc./min.....	2,000	2,000
Ethylbenzene conversion, mol percent.....	34.7	1.2
Selectivity to styrene, percent.....	65	91

As is evident from the foregoing examples, the present technique and apparatus achieves substantially higher conversions and selectivities at a given temperature than are obtainable with ordinary catalytic dehydrogenation processes of the prior art and, more particularly, permit the use of substantially lower dehydrogenation temperatures to effect a commercially significant degree of conversion.

I claim as my invention:

1. Process for the low temperature dehydrogenation of a hydrocarbon feed to form a less saturated hydrocarbon of corresponding structure and free hydrogen, which comprises reacting the feed under dehydrogenation conditions including a temperature of about 800° F. to about 1000° F., maintaining the dehydrogenation reaction mixture in contact with one side of a thin silver membrane, maintaining an oxygen-containing gas in contact with the other side of said membrane under a pressure sufficient to cause oxygen to diffuse therethrough, and diffusing oxygen through the membrane to oxidize said free hydro-

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gen in a filmular oxidation zone adjacent the membrane, thereby lowering the hydrogen partial pressure of the reaction mixture.

2. Process of claim 1 wherein said membrane is tubular in form.

3. Process of claim 1 wherein said reaction is effected in contact with a dehydrogenation catalyst.

4. Process of claim 3 wherein said catalyst is coated on the dehydrogenation side of said membrane.

5. Process of claim 3 wherein said catalyst comprises a bed of particles.

6. Process of claim 3 wherein said catalyst comprises a platinum group metal.

7. Process of claim 1 wherein said hydrocarbon feed is a paraffin containing 3 to 6 carbon atoms per molecule.

8. Process of claim 1 wherein said hydrocarbon feed is a monolefin containing 3 to 6 carbon atoms per molecule.

9. Process of claim 1 wherein said hydrocarbon feed is an alkyl benzene in which the alkyl group contains 2 to 6 carbon atoms.

#### References Cited

#### UNITED STATES PATENTS

2,387,731	10/1945	Allen	260—680
2,431,632	11/1947	Brandt	48—224
2,444,222	6/1948	Craig	48—224
3,290,406	12/1966	Pfefferle	260—683.3

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